Ionic Liquids.

Modern Methods of Synthesis, Polymerization,

Characterization, and Application

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Dipl.-Chem. Nina Gonsior
aus Osnabrück

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Abstract

In the first part of this thesis, the rheology of randomly methylated (1.8) β-cyclodextrin (m-β-CD) dissolved in 1-ethyl-3-methyl imidazolium acetate [EMIM][Ac] was studied in detail by rotational and oscillatory shear measurements. The solutions showed abrupt changes of the structurally dependent rheological moduli and reproducible transitions from gel to sol state at specific shear stresses. A non-Newtonian flow behavior including shear thinning was obtained and analyzed with the Bingham model. Furthermore, the temperature dependence of the viscosity was investigated and the flow activation energies were calculated. A correlation between m-β-CD concentration and flow activation energy could be established.

In chapter 3 to 5, the synthesis of novel ionic liquid derived polyelectrolytes is described. For instance, a water soluble foamable polyelectrolyte was synthesized via free radical polymerization of an ionic liquid derived monomer with *tert*-butyl moiety. Copolymers, obtained by copolymerization with NiPAAm showed a LCST behavior in aqueous solution with T_c values between 34 and 55 °C. Furthermore, a novel cyclodextrin containing polyelectrolyte was synthesized via click reaction as an intriguing polymeric host for smart supramolecular assembling systems. By inclusion complexation of adamantyl carboxylate as a model guest, pseudo-betaine structures with reversible UCST-behavior were obtained and the complex stabilities were determined by isothermal titration calorimetry. In addition, the synthesis of polyelectrolytes by regioselective derivatization of cellulose with three different ionic liquids via click chemistry is presented and the rheological behavior in 1-ethyl-3-methyl imidazolium acetate was studied. A Newtonian flow behavior was recorded and the viscosity was significantly influenced by the ionic moieties compared to the viscosity of unmodified cellulose samples. Furthermore, the viscosity could be controlled by varying the substituents. The viscosity-temperature dependence was analyzed with the Vogel-Fulcher-Tammann equation and the Arrhenius plot, respectively.

In the last section of this thesis the synthesis of a mesomeric betaine via quaternization reaction of 1-butylimidazole and tetrabromo-1,4-benzoquinone was investigated. The structure was verified by X-ray single crystal analysis and the ability to form inclusion complexes with m-β-CD was analyzed by UV-vis spectroscopy. Furthermore, the same reaction conditions were applied to poly(vinylimidazole) and 1,4-di(1*H*-imidazol-1-yl)butane to obtain functionalized polymer networks and oligomers, respectively.

Zusammenfassung

Im ersten Teil dieser Arbeit, wird das rheologische Verhalten von statistisch methyliertem (1.8) β-Cyclodextrin gelöst in 1-Ethyl-3-Methyl Imidazolium Acetat [EMIM][AC] mittels rotatorischer und oszillatorischer Messungen detailliert untersucht. Die Lösungen zeigten abrupte Veränderungen der strukturell abhängigen rheologischen Moduli bei bestimmten Schubspannungen. Darüber hinaus zeigten sie ein nicht-Newtonisches Fließverhalten einschließlich Scherverdünnung, welches anhand des Bingham-Modells analysiert wurde. Über die Temperaturabhängigkeit der Viskosität konnten die Fließaktivierungsenergien berechnet werden.

In Kapitel 3 bis 5 werden die Synthesen und Eigenschaften neuer Polyelektrolyte beschrieben. Durch freie radikalische Polymerisation einer methacrylierten Ionischen Flüssigkeit mit *tert*-Butyl Einheit konnten aufschäumbare Polyelektrolyte erhalten werden. Copolymere mit *N*-Isopropylacrylamid Einheiten zeigten ein LCST Verhalten in wässriger Lösung mit T_c-Werten zwischen 34 °C und 55 °C. Polyelektrolyte mit thermoresponsivem Verhalten und supramolekularen Bindungseigenschaften wurden durch Funktionalisierung und Polymerisation einer methacrylierten Ionischen Flüssigkeit mit Cyclodextrin synthetisiert. Durch Komplexierung von Adamantylcarboxylat als Gast, wurden Pseudo-Betain-Strukturen mit reversiblem UCST-Verhalten erhalten und die Komplexbildungskonstanten mittels isothermer Titrationskalorimetrie bestimmt. Mittels regioselektiver Derivatisierung von Zellulose mit ionischen Flüssigkeiten via Click-Chemie konnten weitere neuartige Polyelektrolyte synthetisiert werden. Das rheologische Verhalten in [EMIM] [AC] wurde untersucht und die Viskosität (η) mit der von unmodifizierter Zellulose verglichen. Durch die Einführung der ionischen Einheiten konnte η signifikant gesenkt und durch Variation der Substituenten eingestellt werden. Die Temperaturabhängigkeit der Viskosität wurde mittels der Vogel-Fulcher-Tammann- bzw. der Arrhenius-Gleichung analysiert.

Im letzten Abschnitt dieser Arbeit wird die Synthese eines mesomeren Betains mit Imidazolium-enolat Struktur aus 1-Butylimidazol und Tetrabrom-1,4-benzochinon beschrieben. Die Verbindung wurde mittels Röntgenstrukturanalyse verifiziert und Einschlussverbindungen mit m-β-CD mittels UV-vis-Spektroskopie untersucht. Für die Synthese funktionalisierter Polymernetzwerke bzw. Oligomere wurde die Reaktion auch mit Poly(vinylimidazol) und 1,4-Di (1*H*-imidazol-1-yl)-butan durchgeführt.

We keep moving forward, opening up new doors and doing new things, because we are curious....

And curiosity keeps leading us down new paths.

Walt Disney - "Keep moving forward"

Contents

Abbreviations

aF^4	asymmetric flow field flow fractionation
AIBN	2,2´-azobisisobutyronitrile
c	concentration
CD	cyclodextrin
C_P	heat capacity
CuAAc	copper(I) catalyzed azide alkyne click reaction
β-CD	β-cyclodextrin
m-β-CD	randomly methylated (1.8) β-cyclodextrin
DLS	dynamic light scattering
DMF	*N*,*N*-dimethylformamide
DMSO	dimethyl sulfoxide
DP	degree of polymerization
DSC	differential scanning calorimetry
E_a	activation energy
[EMIM][Ac]	1-ethyl-3-methyl imidazolium acetate
ESI	electrospray ionization
et al.	et alii
FT-IR	fourier transform infrared spectroscopy
g	gramm
ΔG	free enthalpy
GC/MS	gas chromatography/mass spectroscopy
GPC	gel permeation chromatography
h	hour
ΔH	enthalpy

IL	ionic liquid
ITC	isothermal titration calorimetry
K	Boltzmann constant
kJ	kilojoule
l	liter
LCST	lower critical solution temperature
MALDI-TOF	matrix assisted laser desorption ionization - time of flight
MALS	multi-angle light scattering
min	minute
ml	milliliter
M_n	number average molecular weight
mmol	millimol
mp	melting point
MS	mass spectroscopy
M_w	weight average molecular weight
NiPAAm	*N*-isopropylacrylamide
nm	nanometer
NMR	nuclear magnetic resonance
p.a.	pro analysis
Pa	Pascal
PLM	polarized light microscopy
PS	polystyrene
R	gas constant
RTIL	room temperature ionic liquid
s	second

ΔS	entropy
t	time
τ	transmittance
T	temperature
T_c	critical temperature
T_d	decomposition temperature
T_g	glass transition temperature
T_p	pyrolysis temperature
T_{VF}	Vogel-temperature
TGA	thermogravimetric analysis
UCST	upper critical solution temperature
UV-vis	ultraviolet-visible
V	volume
wt-%	weight percent

NMR-spectroscopy

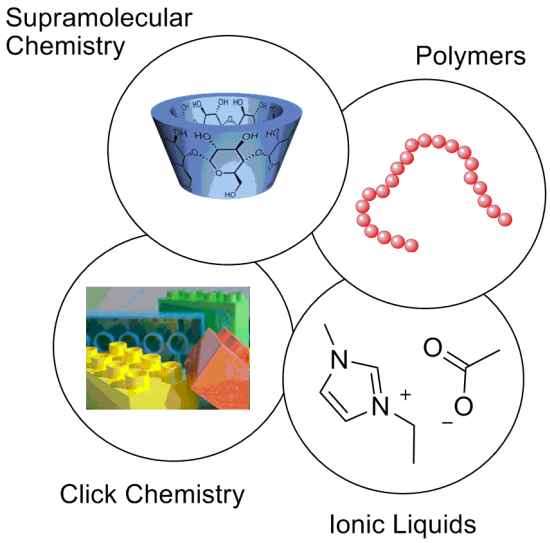
δ	chemical shift
d	doublet
J	coupling
m	multiplet
MHz	megahertz
ppm	parts per million
s	singlet
t	triplet

Rheology

E_η	flow activation energy
f	frequency
G'	storage modulus
G"	loss modulus
LVE	linear viscoelastic
δ	phase shift angle
η	viscosity
$\lvert\eta^*\rvert$	complex viscosity
η_B	Bingham flow coefficient
ω	angular frequency
τ_B	Bingham yield point
τ_0	yield point
τ_r	relaxation time
Á	shear rate

Chapter 1

Introduction to Ionic Liquids, Supramolecular Chemistry, and Click Chemistry within the Field of Polymer Science



Abstract

In the last years, ionic liquids, supramolecular chemistry and click chemistry had enormous impact within the field of polymer science. In this chapter a brief historical overview is given, general aspects are described, and the progress of utilizing these approaches in polymer science and processing is highlighted, respectively.

1 Introduction

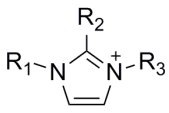
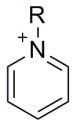
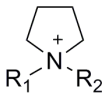
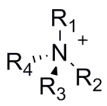
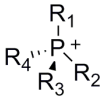
1.1 Ionic Liquids

1.1.1 General aspects

Ionic liquids (ILs) are organic salts mainly composed of organic cations and inorganic anions, which are per definition liquid below 100 °C and exhibit in most cases relatively low viscosities.[1,2] The definition allows distinguishing them from a classical molten salt, which is mostly a high-melting, highly viscous and very corrosive substance.

Conventionally, ILs typically contain bulky asymmetric organic cations, such as imidazolium, pyridinium, pyrrolidinium, quaternary ammonium or tetraalkylphosphonium, with very low symmetry, weak intermolecular interactions and low charge densities.[3-7] Therefore, these cations hinder the regular packing in a crystal lattice. The solid crystalline state becomes energetically less favorable, leading to low melting points.[8] Furthermore, this effect can be enhanced by implementation of anions with a delocalized charge.[9] A selection of typical cations and anions of ILs is given in Table 1.1.

Table 1.1 Schematic representation of selected structures of ionic liquid cations and anions.

Cations	Anions
    	Cl^- / $AlCl_3^-$ Cl^-, Br^-, I^-, $(CN)_2N^-$ NO_3^-, SO_4^{2-}, $EtSO_4^-$ CF_3COO^-, CH_3COO^-, $CF_3SO_3^-$ BF_4^-, PF_6^- $(CF_3SO_2)_2N^-$

The main advantages of ionic liquids are their negligible volatility, their non-flammability, the control of their properties due to the composition, and their high compatibility with various

organic compounds and other materials. Additionally, they can be easily recycled due to their immiscibility with a range of solvents.[10-14] Due to their fascinating and outstanding properties, ILs are often considered as future solvents for catalysis,[15,16] chemical reactions,[17,18] extractions,[19] electrochemical purposes,[20-23] and many other potential applications.[1,4] Of particular interest in this context are room temperature ionic liquids (RTILs), which are already liquid at temperatures below 25 °C.

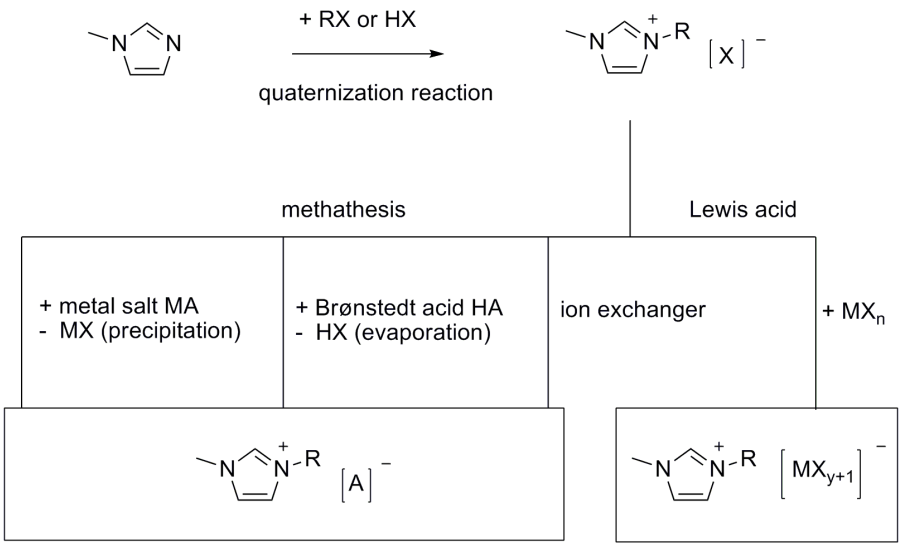
Frequently, ILs are termed "green solvents" or "designer solvents".[10,11,24-27] The reputation of "green solvents" mainly arises from the fact that ILs are non-volatile under standard conditions and therefore do not create atmospheric pollution. By the choice and combination of the ions, physicochemical properties such as polarity, viscosity, solubility, melting point, thermal and electrochemical stability can be targeted. Therefore, ILs are also called "designer solvents" or "task-specific ionic liquids".[1]

The first synthesis of an ionic liquid, ethanolammonium nitrate (mp. 52-55 °C), was reported by Gabriel and Weiner in 1888.[28,29] In 1914, Walden reported on the first room temperature ionic liquid, ethylammonium nitrate (EAN).[30] This polar, colorless liquid exhibits a melting point of 14 °C,[31] is supposed to form three-dimensional hydrogen bond networks[32,33] and has an equal number of donor and acceptor sides. Although it is widely agreed upon as that these findings were the starting point of a new material class of ionic liquids, this paper did not receive much resonance in the scientific world at its time. In the 1970s Osteryoung *et al.* and Wilkes *et al.* for the first time prepared, chloroaluminate melts, which were liquid at room temperature.[3,34-40] However, ILs with anions such as $[AlCl_4]^-$ did not attract much interest for application due to their sensitivity towards hydrolysis. Therefore, it was not before the synthesis of an air and water stable ionic liquid based on an imidazolium cation and either acetate $[CH_3COO]^-$ or tetrafluoroborate [BF4]$^-$ as anion in 1992[3,41] that the interest increased rapidly. The high tolerance of functional groups within the cation choice compared to the chloroaluminate melts opened a much larger range of applications, especially in the field of new high polar solvents. Since 1992, a wide range of ionic liquids has been developed incorporating many different anions including hexafluorophosphate $[PF_6]^-$, acetate, trifluoroacetate $[CF_3COO]^-$, sulfate $[SO_4]^{2-}$, hydrogensulfate $[HSO_4]^-$, organosulfate $[R\text{-}SO_4]^-$, nitrate $[NO_3]^-$, biscyanamide $[N(CN)_2]^{2-}$, trifluoromethanesulfonate $[CF_3SO_3]^-$, bis(trifluoromethylsulfonyl)imides $[Tf_2N]^-$, and tris(trifluoromethylsulfonyl)methanide $[C(CF_3SO_2)_3]^-$. Until today, one million different simple ionic liquids were synthesized.[3] In the last decade more

than 8000 papers have been published in the field of ILs.[24] More than 40 papers published per week underlining the extremely growing interest in this field.[3] Nevertheless, ionic liquids are still relatively expensive and especially imidazolium and pyridinium based ILs show a pronounced cytotoxicity limiting their application in industrial processes.

1.1.2 Preparation of ionic liquids

Principally, the synthesis of ionic liquids includes 1 or 2 steps (Scheme 1.1). The initial step is the quaternization reaction (S_N2-reaction) for example of an amine with an alkylating agent. Typical alkylating agents used are alkane halides. In cases where it is impossible to form the desired anion directly within the first step, two different pathways to vary the anion are possible. The anion-exchange can be realized via Lewis-acid-base reaction or via anion-metathesis.[1,42] Both types of reactions are carried out from the halide salts of ionic liquids. Typical Lewis acids used in this context are $AlCl_3$, BCl_3, $CuCl_2$, $FeCl_2$, or $SnCl_2$.



Scheme 1.1 Synthesis path for preparation of an imidazolium based ionic liquid.[1,42]

It should be noted that it is essential to use purified starting materials, since every impurity highly alters not only the physical but also the chemical properties of these substances, to obtain ionic liquids with high purity. The slightest impurity introduced during the synthesis can hardly be removed, especially when the synthesized salt is a room temperature molten salt.

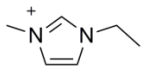
1.1.3 Properties and applications of ionic liquids

The physicochemical properties of ionic liquids can be varied by the selection of suitable cations and anions. Taking this into account, it is possible to optimize the ionic liquid for a specific application. Nevertheless, the physicochemical properties are significantly affected by the purity of the substances and the water content of the IL. Since most ILs are hygroscopic, the accurate determination of some properties e.g. viscosity is a challenging task.

1.1.3.1 Melting points and liquid range of ionic liquids

Since it is well known that the characteristic properties vary with the choice of the cation and anion, the relation between structure of cation and anion and melting point is of particular interest. In general, charge, size, symmetry, intermolecular interaction and delocalization of charge are the main factors that influence the melting point.[1,35,42-47] With increasing size of the anion the Coulomb interactions in the crystal lattice are diminishing and the melting point of the salt decreases. In combination with a good charge delocalization, low solid-liquid phase transition temperatures can be achieved. For example, the melting point of a 1-ethyl-3-methyl imidazolium salt decrease from 87 °C to -14 °C in order of $Cl^- > NO_3^- > BF_4^- > CF_3COO^-$ (Table 1.2).[34,35,41,48,49]

Table 1.2 Influence of the anion size on the melting point.

Salt		Anion size	mp. [°C]	Ref.
	Cl^-	small	87	[34]
	NO_2^-		55	[41]
	NO_3^-		38	[41]
	$AlCl_4^-$		7	[35]
	BF_4^-		6	[48]
	$CF_3SO_2^-$		-9	[49]
	CF_3COO^-	large	-14	[49]

Additionally, for 1-alkyl-3-methyl imidazolium cations the alkyl chain length has a significant influence on the melting point. For example, for an alkyl-chain length up to n = 8 - 10 the

melting point decreases. However, beyond this point, van-der-Waals interactions between the hydrocarbon chains gain more and more importance. The melting point starts to rise with increasing alkyl chain length while the symmetry is decreasing.[42,50]

For most ionic liquids, cooling from the liquid state leads to glass formation at low temperatures as a result of the extremely unfavourable packing-efficiency in the solid state. Usually, the glass transition temperature (T_g) is found to be lower than -50 °C [49,51] and particularly in the range between -70 °C and -90 °C for 1- alkyl-3-methyl imidazolium salts.[42]

In average, ionic liquids have a wide temperature range of liquid state, frequently found from -80 °C up to 300 °C. The melting point represents the lower limit of the liquid range within it is possible to use the salt as a liquid. The upper limit is usually related to the thermal decomposition of ILs since most of them are non-volatile. Until now, the statement that ILs have no vapor pressure has not only theoretically been refuted, even in some cases a distillation of ILs in vacuum is possible.[52,53]

The decomposition temperature (T_d) is mainly influenced by the strength of the incorporated heteroatom-carbon and heteroatom-hydrogen bond.[1] High decomposition temperatures can be provided by ILs whose cations are obtained by quaternization reaction using an alkylating agent, in special cases up to 450 °C.[54] Nevertheless, long time exposure at high temperatures leads to decomposition in most cases.

Table 1.3 Influence of the anion on the decomposition temperature (T_d) for 1-ethyl-3-methyl imidazolium based ILs.[55]

Anion	T_d (onset) [°C]
CF_3COO^-	150
Cl^-	285
I^-	303
PF_6^-	375
BF_4^-	412
$CF_3SO_3^-$	440
Tf_2N^-	455

Furthermore, the thermal stability of ILs is also affected by the present anions. In general, the temperature stability is higher when weak coordinating anions are used (Table 1.3).[44,48,49,55,56]

1.1.3.2 Viscosity

In general, ILs can be classified in terms of their Newtonian or in some cases thixotropic characteristics.[57] The viscosities of ionic liquids are in a range of 10 mPas to 500 mPas at ambient temperature.[4] This is two or three orders of magnitude higher than viscosities of traditional organic solvents.[58] In comparison, the viscosity of water is only 0.89 mPas. The high viscosities are therefore one of the major limiting factors for the large-scale use of ionic liquids.

The viscosity of ILs is essentially influenced by their tendency to form hydrogen bonds and by the strength of their van-der-Waals interactions.[49] The ability of hydrogen bonding is mostly affected by the present anions. Within a series of imidazolium based ILs containing the same cation, an exchange of the anion clearly changes the viscosity in the general order $Tf_2N^- < BF_4^- < PF_6^-$ < halides. Furthermore, for ionic liquids with the same anion the trend of increasing viscosity with increasing chain length of the alkyl substituent, by means of stronger van-der-Waals interactions, has been found.[42,49,59]

Furthermore, the viscosity of many ILs is strongly dependent on temperature. A common way to analyze the viscosity-temperature dependence for non-associating electrolytes is to use the logarithmic form of the Arrhenius equation (Eq. 1),[60] where E_η is the activation energy for viscous flow, R is the universal gas constant and η_∞ is the viscosity at infinite temperature.

$$\ln \eta = \ln \eta_\infty + (E_\eta/RT) \qquad (1)$$

In case of ILs, the Arrhenius law can generally be applied when the cation only presents a limited symmetry.[58,62] If that is not the case, especially in the presence of small and symmetrical cations with low molar mass, the empirical Vogel–Fulcher–Tammann (VFT) equation (Eq. 2), is recommended,[7,60-62] where η_0, B and T_{VF} (Vogel-temperature) are adjustable parameters.

$$\eta = \eta_0 \exp(B/(T-T_{VF})) \qquad (2)$$

1.1.3.3 Solvent properties

Ionic liquids can be described as dipolar, protic or aprotic solvents respectively. To evaluate the solvent polarity dielectric constants, dipole moments and refractive indices are often used as macroscopic physical solvent polarity parameters.[4] A direct measurement of the dielectric constant which requires a non-conducting medium is not available for ionic liquids. Therefore, empirical solvent polarity scales mostly based on solvatochromic or fluorescent dyes are utilized to classify ionic liquids. The most common polarity scale is based on $E_{T(30)}$-values utilizing the solvatochromic shift of the lowest energy π-π* absorption band of the Reichardt´s betaine dye.[63,64] Today, $E_{T(30)}$-values, normalized to water and tetramethylsilane (TMS), are known for more than 360 different solvents and mixtures.[65] The polarity scale of several organic solvents including different groups of ionic liquids is illustrated in Figure 1.1.

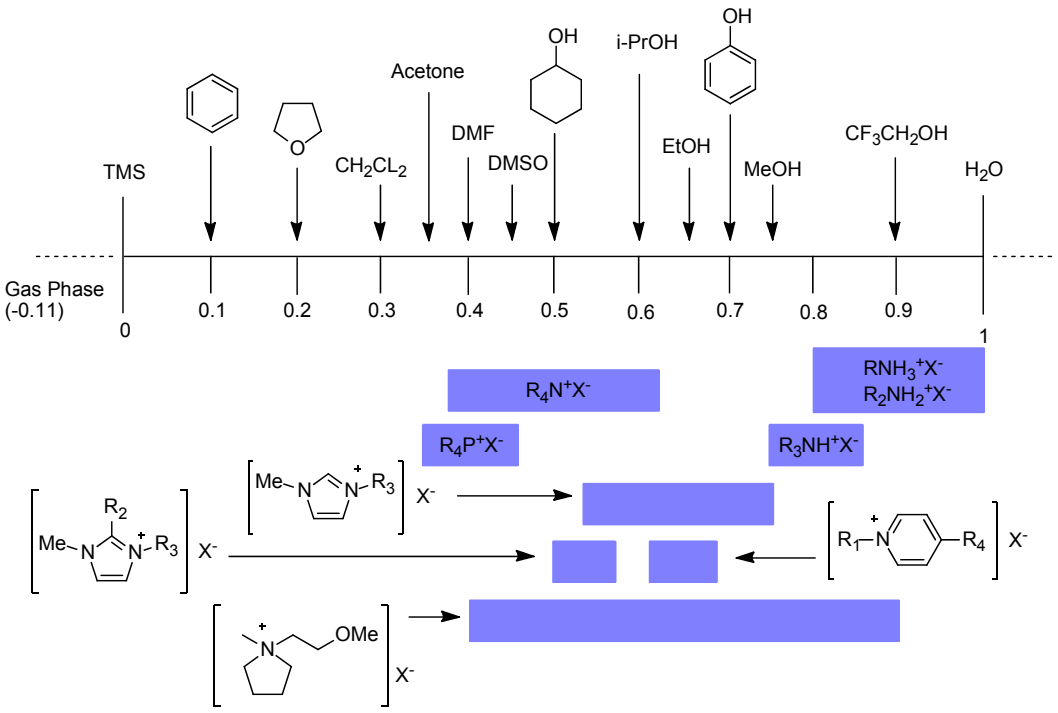


Figure 1.1 Normalized solvent polarity scale for several organic solvents and different groups of ionic liquids.[65]

In the case of ILs based on 1-alkyl-3-methyl imidazolium cations, the polarity is dominated by the present anion for short alkyl chains, whereas for long alkyl chains the influence of the

present anion is decreasing. Furthermore, the polarity decreases in the order of $NO_2^- > NO_3^- > BF_4^- > Tf_2N^- > PF_6^-$ and therefore with anion size and more particular with the effective charge density of the anion.[63] Furthermore, even the solubility in water is significantly affected by the anion for imidazolium based ILs. For this reason these ILs can either exhibit a hydrophilic or hydrophobic character. Anions such as halides, acetates, nitrates and ethylsufates form hydrophilic ILs while anions such as $[PF_6]^-$ and $[Tf_2N]^-$ lead to hydrophobic ILs.[3] Some commonly used anions are summarized in Figure 1.2 with respect to their solubility in water.

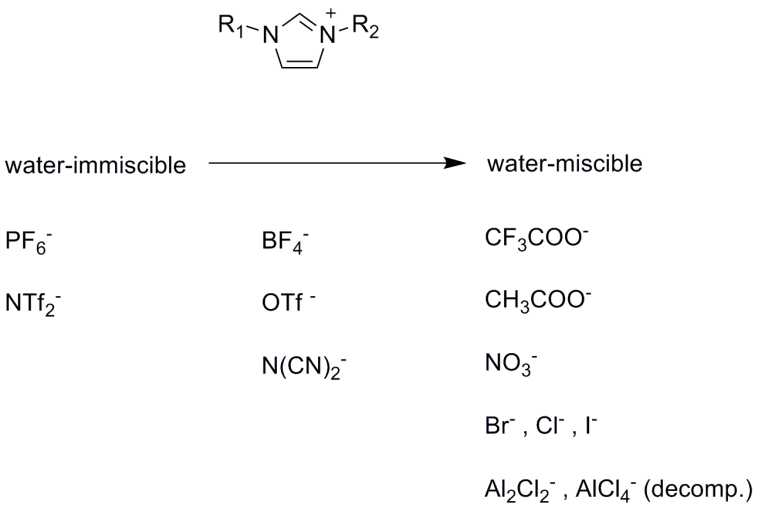


Figure 1.2 Water solubility of imidazolium based ILs depending on the anion.

1.1.3.4 Applications

The outstanding physicochemical properties of ILs render them excellent candidates for a broad range of applications, especially room temperature ionic liquids (RTILs).[24,25,66-68] In fact, at the current level of development, ionic liquids can even replace conventional organic solvents in numerous different applications.[3] In Table 1.4 organic solvents are compared to ILs emphasizing the most important advantages and disadvantages of ILs.

ILs have already been used as catalysts,[69,70] reagents[71] or solvents[72,73] in several chemical reactions. Furthermore, ionic liquids are used in separation processes[74,75] and as electrolyte materials in catalytic processes.[76,77] Great efforts have been made utilizing ILs as solvents

for biopolymers. Especially cellulose the most abundant natural polymer in nature can be dissolved in rather high concentrations (up to 25 wt%) which is not possible in conventional organic solvents.[78] The most efficient solubility can be obtained when imidazolium based ionic liquids with chloride or acetate anions were used, e.g. 1-ethyl-3-methyl imidazolium acetate or 1-butyl-3-methyl imidazolium chloride. These anions are nonhydrated and can disrupt and break the intramolecular hydrogen bonds of the cellulose network without derivatization.[78-80]

Table 1.4 Brief comparison of organic solvents with ionic liquids.[3]

property	organic solvents	ionic liquids
number of solvents	> 1000	> 1 000 000
applicability	single function	multifunction
cost	normally cheap	2-100 times higher costs
recyclability	green imperative	economic imperative
catalytic ability	rare	common and tuneable
chirality	rare	common and tuneable
flammability	usually flammable	usually non-flammable
solvation	weakly solvating	strongly solvating
vapor pressure	usually remarkable	negligible
viscosity [mPas]	0.2 - 100	22 - 40 000

Beside the usage of ILs as solvents for organic reactions, the application as electrolytes in lithium batteries,[20,81] in electroplating processes,[82,83] and solar cells[84-87] reflects the applicability in electrochemistry. Remarkable are also the investigations of ionic liquids with regard to their advantages in formulation technology, in colloid science and in tribology during the last years. ILs can be utilized e.g. as additives in paints, for improved finish and drying processes,[88] as templates in nanotechnology[89-96] or as innovative lubricants for steel on aluminium applications.[97,98] An overview of the diversity of IL applications is given in Figure 1.3.

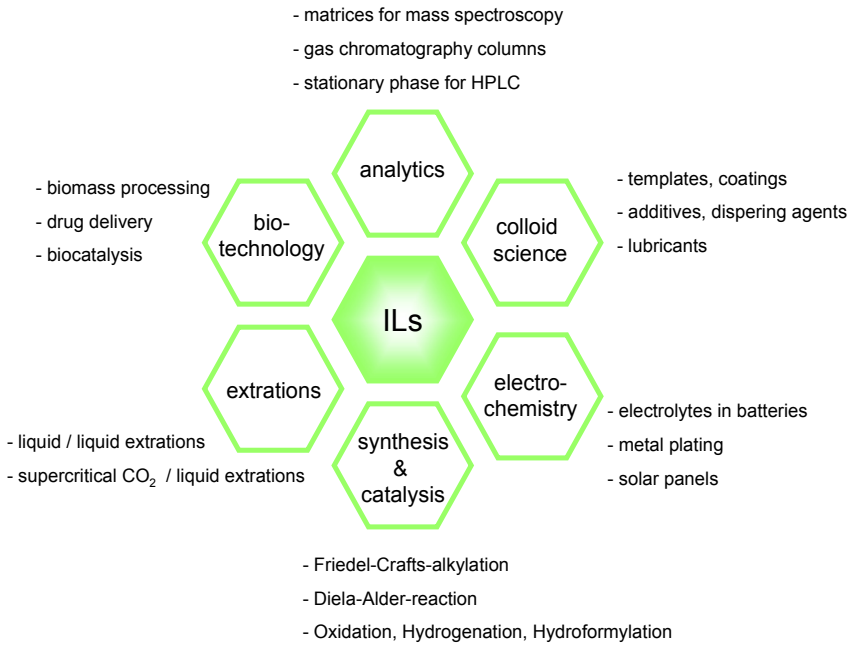


Figure 1.3 General survey of recent applications of ionic liquids.

In the last years several industrial applications have been developed.[3] Currently, the most successful example for an industrial process involving an ionic liquid is the BASIL™ (Biphasic Acid Scavenging utilizing Ionic Liquids) process which was introduced by BASF AG in 2002. It is used for the production of alkoxyphenylphosphines. In the original process chart, triethylamine was used as acid scavenger yielding triethylammonium chloride as solid waste product. By replacing triethylamine with 1-methylimidazole, the ionic liquid 1-methylimidazolium chloride is obtained, which separates from the reaction mixture as a discrete phase. The yield increased from 50 % to 98 % and the IL could be further recycled via base decomposition yielding 1-methylimidazole.[99] Beside the BASIL™ process, BASF AG demonstrated, that hydrogen chloride solubilized in ionic liquids could act as phosgene substitute. A reaction mixture of 1,4-dihydroxybutane and HCl/IL results in an almost pure 1,4-dichlorobutane (98% selectivity) product. In contrast, the direct reaction without ionic liquids produced a reaction mixture of four products with 1,4-dichlorobutane only as a minor by-product.[100]

1.1.4 Ionic liquids in polymer chemistry

In recent years, ILs have been used in polymer science, mainly as polymerization media in several types of polymerization processes including free radical polymerizations,[101] atom transfer radical polymerizations (ATRP),[102-107] reversible addition-fragmentation transfer (RAFT) polymerizations,[108] as well as in ionic and coordination polymerizations.[109,110]

The utilization of ionic liquids as solvents in polymerization processes can provide several advantages.[104,111] In general, a significant increase of k_p/k_t ratio was observed for free radical polymerizations conducted in ILs compared to those carried out in other polar/coordinating solvents. Beside radical polymerization processes, also coordination polymerization, condensation polymerization, electrochemical polymerization and enzymatic polymerization processes can benefit from the utilization of ILs. Major advantages were i.e. mild reaction conditions, reuse of catalytic systems without loss of activity, higher yields, high enzyme activity, and the synthesis of high conductive polymer films.[111]

However, the use of ILs in polymer science is not only limited to polymerization media. ILs have also been investigated as monomers which result in novel solid polyelectrolytes having ILs moiety in the polymer structure.[112] Ohno *et al.* synthesized a series of polyelectrolytes by polymerization of ionic liquid-based monomers.[112-118] In general, a polymerizable vinyl group was covalently introduced to the cation or (and) anion moiety of an ionic liquid. A variety of polymerized IL systems such as polycations,[116] polyanions,[115] copolymers,[115], poly(zwitterion)s,[116] and (cross-linked) ionic gels[112,119] could be obtained (Figure 1.4). However, in comparison to ILs the ionic conductivity of polymerized ILs was considerably lower due to suppressed mobility of the component ions, but was still higher than those of ordinary polyelectrolytes.

In general, ionic liquid-derived polymers are solids with high melting points or decomposition temperatures, but in some cases liquid polyelectrolytes were obtained. One of the first liquid polymerized IL was synthesized by Ricks-Laskoski and Snow.[120] 2-Acrylamido-2-methyl-1-propanesulfonic acid was mixed with tris[2-(2-methoxyethoxy)ethyl]amine to obtain the quaternary ammonium compound. After polymerization, a clear liquid was obtained at ambient temperature. Furthermore, the polymerization of 11-(1-methyl-imidazolium-3-yl-) undecylacrylate tetrafluoroborate led to a low-melting (38–42 °C) waxy solid [121,122], which can not only be used as a cationic polyelectrolyte, but also as a very effective bactericide.

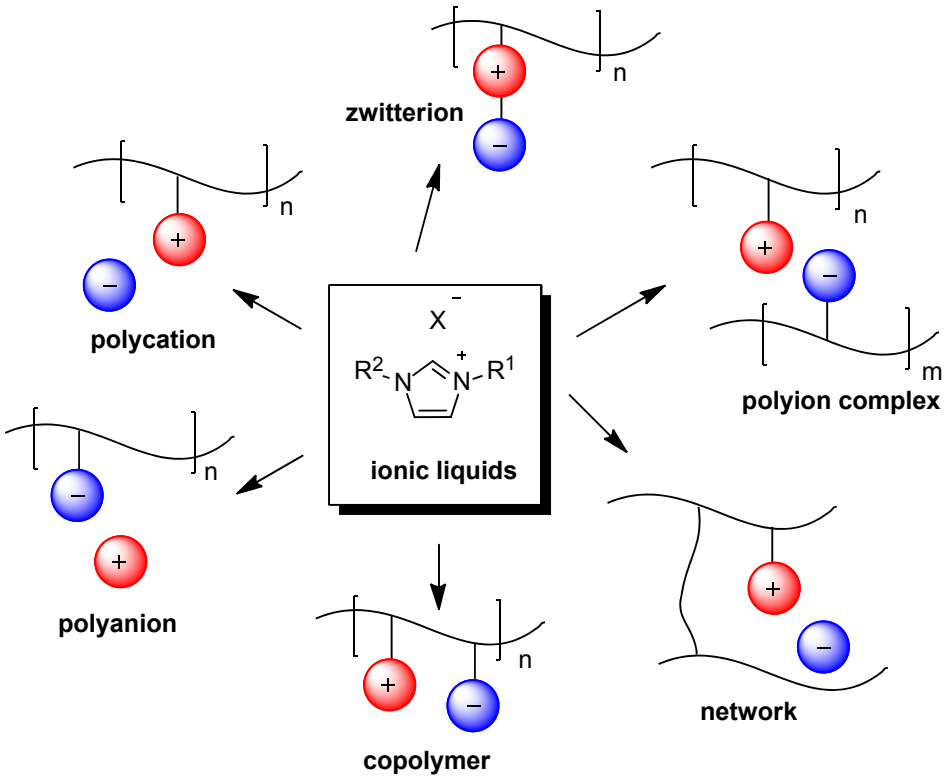


Figure 1.4 Variety of polymerized ionic liquids [112]

In the field of supramolecular chemistry, IL-derived polyelectrolytes showed an interesting behavior in the presence of cyclodextrins. For instance, the water solubility of 1-butyl-3-vinylimidazolium bis(trifluoromethylsulfonyl)imide [BVIM][Tf2N] could be improve by complexation of the anion with randomly methylated β-cyclodextrin (β-CD).[123] However, a spatial separation of the ion pair was received, creating quasi "naked" vinylimidazolium cations which could not be polymerize by free radical polymerization in water. Only in the presence of a foreign salt the cation-cation repulsion could be compensated and the polymerization occurred. Furthermore, the obtained polymer showed a pseudo-LCST (lower critical solution temperature) behavior.[124] At higher temperatures the CD ring separates from the anion and the polymer was insoluble in water again.

1.2 Supramolecular Chemistry

1.2.1 General introduction to supramolecular chemistry

This chapter intends to describe the principles and perspectives in the field of supramolecular chemistry. Importance of this field has grown exponentially in the last few decades as indicated by the large number of articles, reviews, and books. Especially host-guest interactions concerning cyclodextrins are discussed in detail.

Supramolecular chemistry has been defined as the "chemistry of molecular assemblies and the intermolecular bonds" or more colloquially as "chemistry beyond the molecule". Further definitions include phrases such as "the chemistry of the non-covalent bond" and "non-molecular chemistry".[125-129] Originally, supramolecular chemistry was defined in terms of non-covalent interaction between a "host" and a "guest" molecule. Figure 1.5 depicts the relationship between molecular and supramolecular chemistry in terms of both structure and function. One of the most important aspects of supramolecular chemistry is the understanding and the ability to utilize non-covalent interactions for the thermodynamically controlled and reversible assembly of functional moieties.

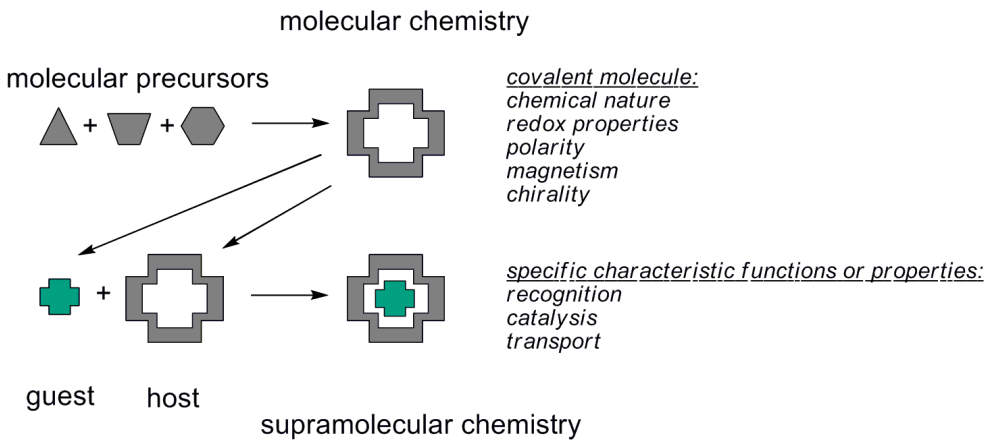


Figure 1.5 Comparison between the scope of molecular and supramolecular chemistry according to ref. [125]

Early inspiration for the construction of supramolecular compounds was obtained from nature and especially from biological aggregates like lipid bilayers, cell membranes, viral capsids, the tertiary and quaternary structure of proteins, and mainly the DNA double helix.[131,132]

In 1894, Fischer reported that sugar-metabolizing enzymes had the distinct ability to recognize various sugars of specific shape.[133] This discovery led to the lock and key hypothesis, pre-empting the concepts of molecular recognition and host-guest chemistry, where binding efficiency and selectivity are maximized by a host whose cavity is pre-formed in a shape to accommodate a specific guest ligand. Eighty years later in 1974, Cram coined the name host-guest chemistry to describe large macrocyclic hosts that envelop smaller guests through well placed complementary interactions.[134] Pioneers in this field are Cram,[134] Lehn[135-138] and Pedersen.[139,140] Their work on crown ethers and cryptands in the area of host-guest chemistry has been awarded with the Nobel Prize for chemistry in 1987. Of these three laureates, Lehn is generally credited with the synthesis of the first supramolecular polymers,[141,142] which were self-assembled chains of small molecules, held together by reversible non-covalent interactions.[143-146] Since then a broad range of macrocycles were used as host in terms of supramolecular chemistry. For example, cyclodextrins,[147] calixarenes,[148-150] cucurbiturils,[151-154] and crown ethers can be synthesized in large quantities, and are therefore convenient for use in supramolecular systems. More complex structures like cyclophanes, and amine-based cryptands[155] and porphyrins[156-158] provided more tailored recognition properties.

Nowadays, the area of supramolecular chemistry ranges from molecular self-assembly, folding, molecular recognition, host-guest chemistry, mechanically-interlocked molecular architectures, to dynamic covalent chemistry.[159]

1.2.2 Interactions in host/guest systems

As already described, supramolecular chemistry concerns non-covalent bonding interactions. The term "non-covalent"[130] contains an enormous range of intermolecular interactions, which, however, originate from only a few attractive and repulsive forces which are listed in order of increasing strength (ΔH) in the following:[126,160-164]

- Van-der-Waals forces (< 5 kJ mol^{-1}, e.g. cyclodextrin inclusion compound).
- dipole-dipole interaction (5 - 50 kJ mol^{-1})
- charge donor-acceptor interactions
- π-π stacking (0 - 50 kJ mol^{-1})
- hydrophobic-hydrophilic interactions,
- hydrogen bonding (4 - 120 kJ mol^{-1})
- electrostatic interactions, (100 - 350 kJ mol^{-1}, e.g. ion-ion, ion-dipol, dipol-dipol) and metal coordination (e.g. crown ether - alkali ion complex)

Hydrogen bonds are a subset of dipole-dipole interactions between electron rich H-bond acceptors (O, N, F) and electron deficient hydrogen atoms and are prevalent in host-guest chemistry, especially for cyclodextrin inclusion compounds. The strength of an H-bond is dependent on electronic effects and the ability of the H-bond acceptor to adapt in the correct spatial orientation.[129] Although a single interaction is generally much weaker than a covalent bond, the cooperative action of many of such interactions may lead to supramolecular species that are thermodynamically and kinetically stable under various conditions.

Many techniques have been employed to study the effect of different structural and medium variables on complexation with CDs. Through determination of the binding constant K_a (stability constant) the thermodynamic parameters responsible for the inclusion process, and the molecular structure the complexes can be characterized. Besides most common spectroscopic methods (NMR, IR, UV-vis),[165] isothermal titration calorimetry (ITC) is an effective analytical tool for host-guest complexes, especially for those including cyclodextrins. The method is useful for K_a values in the range of 10^2 to 10^8. The heat changes (q) from titrating the guest solution into the host solution (e.g. cyclodextrin) or vice versa are measured and the titration curve is fitted using the Wiseman isotherm (Eq. 3),

$$Q = \frac{n \cdot M_t \cdot V\Delta H}{2} \cdot \left[\left(1 + \frac{1}{n \cdot M_t \cdot K} + \frac{X_t}{n \cdot M_t} \right) - \sqrt{\left(1 + \frac{1}{n \cdot M_t \cdot K} + \frac{X_t}{n \cdot M_t} \right)^2 - \frac{4 \cdot X_t}{n \cdot M_t}} \right] \quad (3)$$

where n is the stoichiometry, M_t and X_t are the amount of host and guest respectively in the cell, and ΔH is the enthalpy of titration (and dilution). The mathematical fitting of the titration data is stoichiometry dependent and therefore is a secondary determination of the stoichiometry of the system being explored. However, it has to be taken into account that the heat of dilution correction is significant for guest titrants and is estimated by titration into neat solvent.

1.2.3 Cyclodextrins as a host in supramolecular chemistry

Cyclodextrins (CDs) were first isolated by Villiers in 1891. He discovered the formation of an oligosaccharide, when starch was enzymatically cleaved.[166] In 1904 Schradinger confirmed the results and identified the cyclic structure.[167] However, the correct chemical structure of CD was published in 1938, when Freudenberg characterized them as cyclic structures composed of α-1,4-linked glucose units.[168] It was not until 1953 that Cramer and French recognized and studied possible applications by forming complexes with CDs.[169] Ever since, the interest on cyclodextrins as enzyme models has been aroused.[170-174] Today, the use of CDs as a receptor in supramolecular chemistry led to widespread applications, e.g. chromatographic separations,[175] drug delivery systems,[176,177] food industry,[178-180] solubilisation of environmental pollutants,[181] molecular reactors for mediation of organic reactions[182] or polymerisations[183] and optical sensors.[184,185]

CDs can be obtained biotechnologically in large scale by the enzymatic degradation of starch.[186] In this process cleavage of a turn from the starch helix is followed by intramolecular cyclization[187] leading to cyclic oligosaccharides which consists of (α-1,4)-linked α-D-glucopyranose units. The number of glucose units reflects the cyclodextrin nomenclature. Therefore, the three major natural forms of CDs are termed α-, β- and γ-CD, representing the glucose hexamer, heptamer, and octamer, respectively. Although higher homologues with n > 8 occur in nature, they can not be isolated on an industrial scale in homologous pure form. However, in laboratory scale the synthesis of CDs containing 9-12 glucose units were already

reported.[188] Recently, even large-ring CDs containing as many as 35 residues were synthesized.[189] In general, natural α, β, and γ-cyclodextrins are the most characterized ones with respect to their physical and chemical properties. In Table 1.5 some important properties are summarizes.[187]

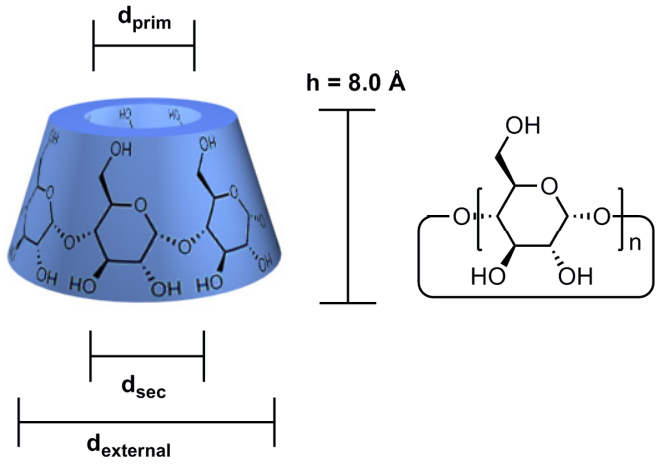
Table 1.5 Some properties of native CDs.

	α-CD	β-CD	γ-CD
number of glucose units	6	7	8
molecular formula	$C_{36}H_{60}O_{30}$	$C_{42}H_{70}O_{35}$	$C_{48}H_{80}O_{40}$
molecular weight [g/mol]	972	1134	1296
melting temperature range [°C]	225-260	255-265	240-245
water solubility at 24°C [g/100ml]	14.5	1.85	23.2
crystal water content [wt%]	10.2	13-15	8-18
water molecules in cavity	6	11	17

Due to the $^4C_1$-chair conformation of the glucopyranose units, cyclodextrins are shaped like a truncated cone rather than perfect cylinders. The hydroxyl functions are orientated to the cone exterior with primary hydroxyl groups located at the side of the narrow inlet, while secondary hydroxyl groups are found at the reverse side (wide inlet). The central cavity is lined by the skeletal carbons and ethereal oxygens of the glucose residues, which gives it a lipophilic character (Figure 1.6).

Due to their structural properties, natural cyclodextrins in particular β-CD, are of limited aqueous solubility and were insoluble in most organic solvents. Substitution of any of the hydrogen bond forming hydroxyl groups, results in a dramatic improvement in their aqueous solubility. A variety of functionalized CDs have been prepared with either hydrophobic (e.g. methyl, propyl) or hydrophilic (sulfate, phosphate, quaternary amine) groups. Water-soluble cyclodextrin derivatives of commercial interest include the hydroxypropyl-derivatives of β-CD and γ-CD, the randomly methylated β-CD, and the sulfobutylether β-CD sodium salt.

Furthermore, cyclodextrins are stable under alkaline conditions but they can, however, be cleaved into glucose by acid hydrolysis.



	d_{prim}	d_{sec}	$d_{external}$
α-CD, n = 6	4.7 Å	5.2 Å	14.6 Å
β-CD, n = 7	6.0 Å	6.4 Å	15.4 Å
γ-CD, n = 8	7.5 Å	8.3 Å	17.5 Å

Figure 1.6 General structure and formula of natural α, β, and γ-CD and the values of the cavity size determined by W. Saenger from CPK models.[187] (n represents the number of glucosepyranose units of cyclodextrin, d is the diameter and h is the height of each cavity)

Because of the relatively apolar cavity in comparison to the polar exterior, cyclodextrins can form inclusion compounds with hydrophobic guest molecules in aqueous solutions, predominantly due to hydrophobic interactions.[190,191] Such inclusion complexes have shown high potential either in theory or in application. The "driving force" of these host-guest processes is a combination of various effects depending on the guest and the CD[192] and are explained in detail in literature.[193] One of the most influential factors on the ability of CDs to form inclusion complexes is the geometric compatibility between the CD cavity and guest species (also know as *complementarity*). The geometric factors are decisive on the types of guest molecules which can penetrate the CD cavity and they determine the "tightness of fit" of the included guest and the CD cavity.[194,195] However, complexation is possible with compounds significantly larger than the cavity dimensions of CDs, but in this case, only certain groups or side chains actually penetrate the host cavity. Inclusion in CDs exerts a profound effect on the physicochemical properties of guest molecules as they are temporarily locked or caged within the host cavity. This gives rise to beneficial modifications of guest molecules, which are not

achievable otherwise. These properties include solubility enhancement of highly insoluble guests, stabilisation of labile guests against the degradative effects of oxidation, visible or UV light and heat as well as the control of volatility and sublimation. Furthermore, taste modification by masking off flavours, unpleasant odours and controlled release of drugs and flavours can be achieved.

Polymers with covalently linked cyclodextrins are known as CD-polymers and are divided into two classes. In Figure 1.7, both types are compared schematically. Branched CD-polymers were synthesized already in 1965 by Solms *et al.*[196,197] through cross-linking of CD with epichlorohydrine in alkaline media. Those water soluble materials were the first reported CD-polymers, and were used to prepare supramolecular structures based on host-guest interactions with suitable guests.

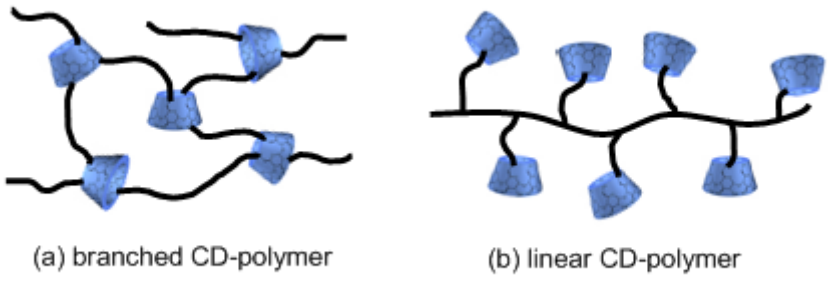


Figure 1.7 Schematic structure of CD-polymers.

In linear polymers CDs are mostly linked with the polymer backbone through spacers. The first cyclodextrin side chain polymers were described by Nozakura *et al.*.[198-200] For the synthesis of these polymers, CD was functionalized with a polymerizable group and polymerized afterwards.[201] The complexation ability of CD-polymers in general differs from that of free cyclodextrins. In most cases, due to steric effects the complex formation constant K_s is humiliatingly low, but remains in the same order of magnitude.[196,200,202] In some exceptional cases, however, it can be also increased considerably.[203] Cooperative effects of adjacent cyclodextrins could be a cause for this unexpected observation.[200]

Besides the two classes of CD-polymers, CDs were often used to thread over polymers to form supramolecular polyrotaxane structures.[162,204-208] Furthermore, Ritter *et al.*[209] described

the synthesis of linear and cyclic supramolecular structures based on CD-dimers as a host and adamantyl-dimers as a guest (Figure 1.8).

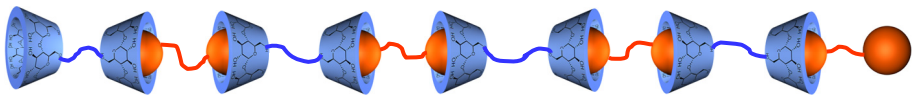


Figure 1.8 Proposed supramolecular structure for CD/adamantyl-dimers

To date more than 1800 papers and around 200 reviews have been published in the context of cyclodextrin and polymer (sciFinder search, deadline: 28th May 2010). Furthermore, the numbers of 940 registered patents reveal the importance of cyclodextrin in polymer chemistry for industrial applications.

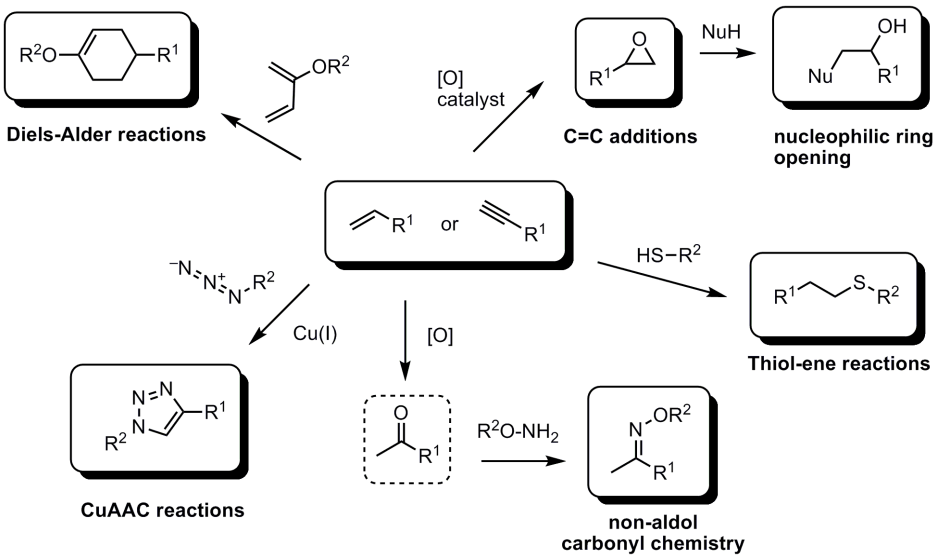
1.3 Click Chemistry

1.3.1 General aspects

Nature has an overall preference to form carbon-heteroatom bonds over carbon-carbon bonds, e.g. in DNA, proteins and polysaccharides.[210] Inspired by nature the concept of click chemistry was introduced by K. B. Sharpless *et al.* in 2001 as a modular synthetic approach towards the assembly of new molecular entities through heteroatom links (C-X-C). They defined click chemistry as reactions that ‘‘*are modular, wide in scope, high yielding, create only inoffensive by-products (that can be removed without chromatography), are stereospecific, simple to perform and that require benign or easily removed solvent*’’.[210,211] Furthermore, a high thermodynamic driving force is required (usually above 20 kcal mol^{-1}), ensuring that the reaction proceeds rapidly, with complete conversion, and shows high selectivity towards a single product. Click chemistry is therefore not a new type of chemistry, but rather a term used for a class of reactions that can create complex molecules in a very efficient manner.

The expanding list of click reactions can be divided into four categories[212] and is further described in Figure 1.2:

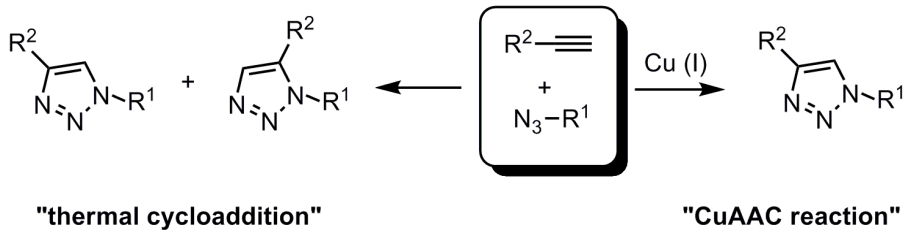
- cycloadditions of unsaturated species such as Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) and Diels-Alder reactions;
- nucleophilic substitution chemistry, involving particularly ring-opening reactions of strained heterocyclic electrophiles such as epoxides, aziridines, aziridinium ions, and episulfonium ions;
- carbonyl chemistry of the non-aldol type such as formations of ureas, thioureas, aromatic heterocycles, oxime ethers, hydrazones, and amides;
- additions of carbon–carbon multiple bonds such as epoxidations, dihydroxylation, aziridination, sulfenyl halide addition, and Michael additions of Nu-H reactants.



Scheme 1.2 A selection of reactions which match the click chemistry criteria.[216]

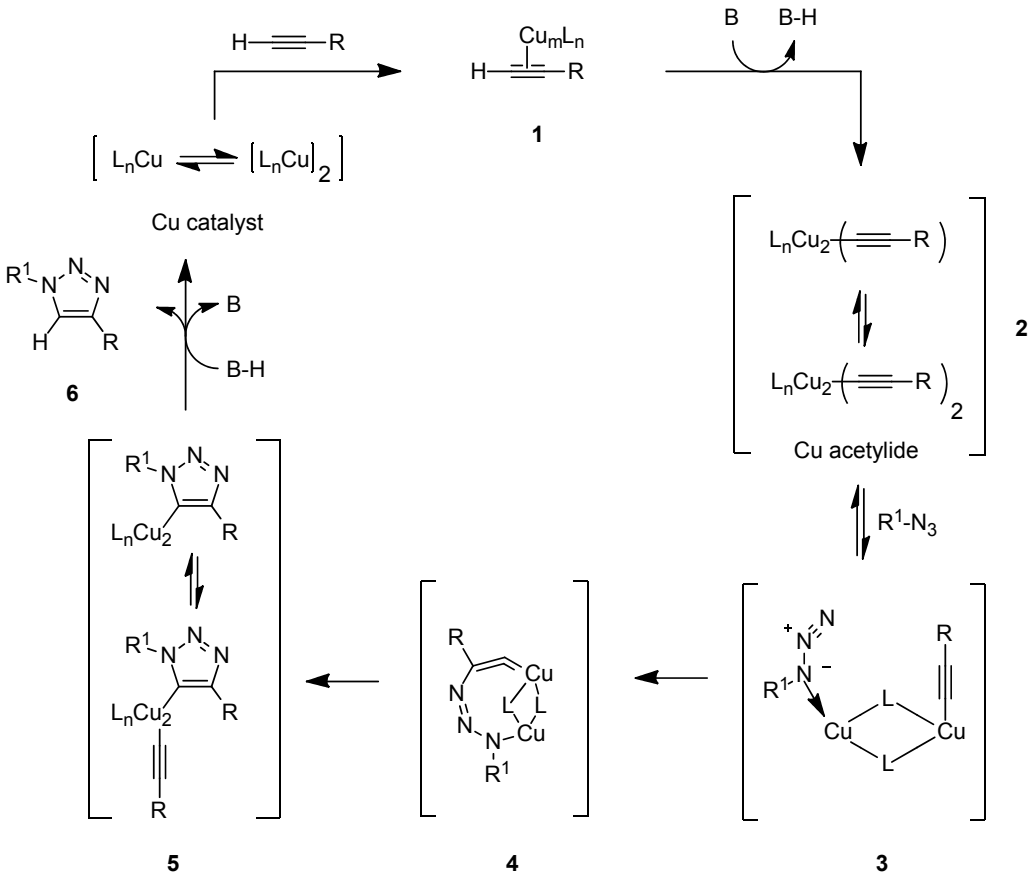
Of all currently identified click reactions, the 1,3-dipolar cycloaddition of alkynes and azides to yield 1,2,3-triazoles is undoubtedly the premier example of a click reaction. The synthesis was discovered by Michael[213] at the end of the 19th century and significantly advanced by Huisgen in the 1960s.[214,215] The high kinetic stability of azide and alkyne groups, meaning that they are inert under a wide range of conditions and do not interact with water, oxygen,

biological molecules or other functionalities was disadvantageous for the reaction. Therefore, the reaction requires long reaction times, high temperatures and result in the formation of 1,4- and 1,5-regioisomers. It was the recent discovery of the dramatically acceleration of the reaction rate up to 10^7 and the increase in regioselectivity towards the 1,4-regioisomer (Scheme 1.3)[217-219] under copper(I) catalysis that has led to its widespread application in nearly all fields of modern chemistry, e.g. molecular biology, drug design, biotechnology, macromolecular chemistry or materials science.[220-232] In the last ten years more than 2000 papers and 190 reviews have been published and at least 120 patents have been registered in the field of click chemistry (sciFinder search, "click chemistry", deadline: 28th May 2010).



Scheme 1.3 The Cu(I) catalysed azide-alkyne click (CuAAC) reaction results in exclusive formation of the 1,4-disubstituted 1,2,3-triazole, whilst the thermally induced Huisgen cycloaddition results in an mixture of 1,4- and 1,5-stereoisomers.[216]

A mechanistic picture of the copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) was first proposed by Meldal *et al.*[217] and Sharpless,[217] further determined by computational methods[233,234] and finally revised by van Maarseveen *et al.*[222] (Scheme 1.4). Briefly, the catalytic cycle begins with the formation of a Cu(I) acetylide species via the π complex **1**. Furthermore, the formation of complex **2** is assumed, since the coordination of copper lowers the pKa value of the alkyne C-H bond, making deprotonation in aqueous solution possible without the addition of a base. The second copper atom is required for the activation of the acetylide towards cyclization by reducing the alkyne electron density. In the next step, the copper acetylide-azide complex **3** undergoes cyclization and formation of metallocycle **4** due to the nucleophilic attack of an acetylide carbon by the azide group. Finally, ring contraction occurs and protonation leads to the final product **6** and regenerates the catalyst.



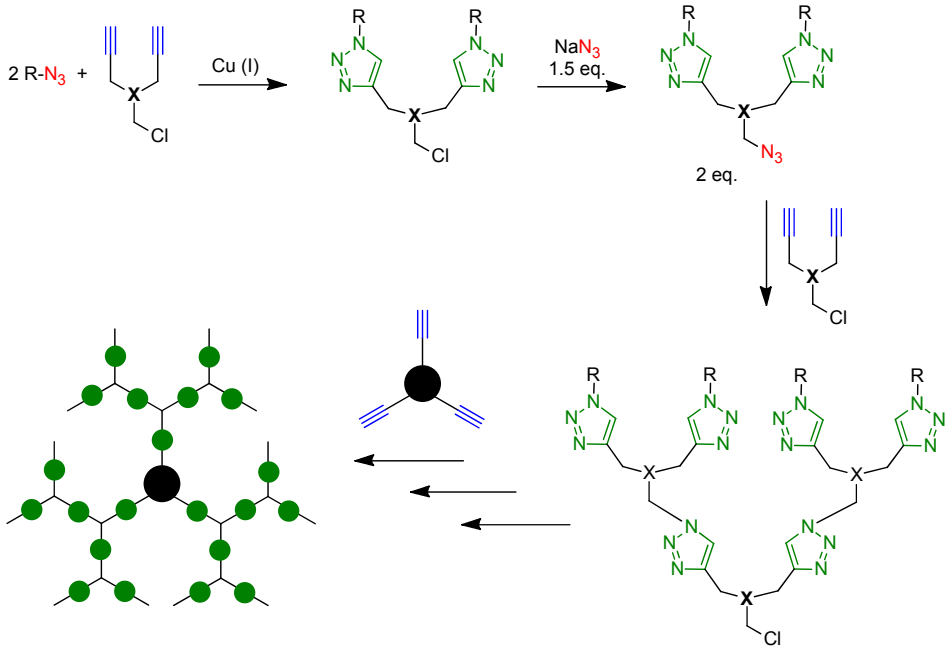
Scheme 1.4 Proposed mechanism for the CuAAc reaction.[222]

1.3.2 Click chemistry in polymer science

Although, the "click" approach originally was introduced for small organic molecule synthesis, this strategy, especially the CuAAC reaction, had enormous impact within the field of polymer science. Since the first approach in polymer science, when Hawker, Fokin, and Sharpless *et al.*[231] employed the reaction during convergent dendrimer preparation (Scheme 1.5), around 430 papers have been published and more than 50 reviews[210,224,235-244] and 30 patents have appeared, emphasizing the importance of this reaction in the field of polymer science.

The application of CuAAC click chemistry in polymer synthesis may be divided into three major categories depending on the requirements of the reaction performance. There is a large number of reports concerning the connection of polymer fragments to form linear, star or

branched block copolymers. Another application is the derivatization of functional sites along the polymer chain or specifically at the polymer end. The third application is the synthesis of cross-linked polymers with well defined structure, super adhesives and materials with fluorescent and electronic properties. As the different applications were already reviewed in detail elsewhere,[245] the following examples will briefly summarize the advantage of the CuAAC reaction in supramolecular CD chemistry and polysaccharide chemistry.



Scheme 1.5 General method for convergent dendrimer synthesis via CuAAC, as initially reported by Hawker, Sharpless, and Fokin *et al.*.[231]

Recently, Ritter *et al.* described the synthesis of supramolecular CD containing copolymers via CuAAC with interesting applications in terms of host guest interactions,[246] polyelectrolytes and hydrogels[247] or drug delivery systems[177]. Therefore, mono-(1*H*-1,2,3-triazol-4-yl)(methyl)2-methylacryl-β-cyclodextrin was synthesized by microwave assisted click reaction of propargyl methacrylate and mono-(6-azido-6-deoxy)-β-CD and further copolymerized with *N*-isopropylacrylamide (NiPAAm).

The synthesis of well-defined 7-arm and 21-arm poly(NiPAAm) star polymers possessing β-CD cores via combination of atom transfer radical polymerization (ATRP) and click reactions

of alkynyl-terminated linear PNiPAAm of varying DPs with β-CD-$(N3)_7$ and β-CD-$(N3)_{21}$, respectively has been described by Liu *et al.*.[248]

Polyrotaxanes, in which CDs were threaded onto poly(ethylene glycol) (PEG) chains capped with β-CDs, were prepared by click chemistry via one-pot strategy in water at room temperature with high yield.[249] The terminal β-CD cavity could be recognized by phenolphthalein and utilized to form a supramolecular block copolymer with alternate rod and coil segments via the formation of a host-guest inclusion complex with diadamantyl-terminated PEG.

Another interesting approach of CuAAC in supramolecular polymer chemistry was described by García Fernández *et al.*.[250] Gene delivery systems based on the β-cyclodextrin scaffold have been synthesized by combining the CuAAC and an efficient acylation method of the secondary hydroxyls. The jellyfish-like structure of the obtained amphiphilic CD-scaffolded "click clusters" is depicted in Figure 1.9.

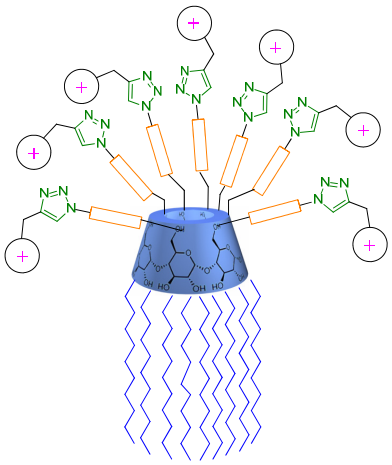


Figure 1.9 Schematic representation of β-CD-scaffolded amphiphilic polycationic "click clusters". The rectangular boxes account for additional spacer elements.[250]

In the field of polysaccharide chemistry, the Cu(I)-catalyzed azide/alkyne click reaction has been proven to be an appropriate strategy for cellulose modification.[251] In contrast to polysaccharide esterification, no cross-linking occurred and hydrolytically stable products could be observed. Therefore, multifunctional cellulose materials were obtained via CuAAC by the regioselective introduction of various compounds, e.g. methylcarboxylate, 2-aniline, and 3-

thiophene moieties,[251] sugar residues,[252] fluorophores,[253] dendrons,[254] as well as anionic,[255] and cationic[256] moieties. Furthermore, nanoplatelet gels and hydrogels could be obtained by chemical cross-linking of azide and alkyne bearing cellulose derivatives via click chemistry.[257-259]

1.4 Aim and Outline of this thesis

Polymers have a great impact on our daily lives and today over 30 million tons of synthetic polymers are produced every year. For instance, they are used as plastics, fibers, rubbers, films, paints, membranes, and adhesives. To develop new applications, the demands on polymers are constantly increasing. Therefore, the utilization of new methods for polymer processing and synthesis as well as alternative reaction media is needed to obtain new high performance polymers. In this context, ionic liquids have been proposed as alternative solvents or ideal starting materials for the synthesis of polyelectrolytes due to their intriguing properties. Furthermore, click chemistry and supramolecular chemistry had enormous impact on the design of polymer structures and therefore on the specific properties for further applications.

The aim of this dissertation is the synthesis of novel ionic liquid derived polyelectrolytes with specific properties in the field of supramolecular chemistry, rheology, foams or dyes. The approach of click chemistry should be applied to both, monomer synthesis and polymer modification. Furthermore, the rheology behavior of CD dissolved in ionic liquids should be investigated for further application as a new solvent-system for the polymerization of nonpolar monomers. Based on these challenging aims the following topics are processed:

- Rheological behavior of cyclodextrin dissolved in ionic liquids
- Synthesis and properties of ionic liquid derived foamable polyelectrolytes
- Synthesis of novel cyclodextrin containing polyelectrolytes via click chemistry to obtain novel polymeric hosts for smart supramolecular assembling systems
- Synthesis of novel polyelectrolytes based on cellulose and ionic liquids via click chemistry and their rheological behavior
- Synthesis of novel mesoionic polymers and oligomers with imidazolium-enolate structure

1.5 References

[1] P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* **2000**, *39*, 3772.

[2] R. D. Rogers, G. A. Voth, *Acc. Chem. Res.* **2007**, *40*, 1077.

[3] N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* **2008**, *37*, 123.

[4] T. Welton, *Chem. Rev.* **1999**, *99*, 2071.

[5] P. Wasserscheid, *Chemie in unserer Zeit* **2003**, *37*, 52.

[6] J. S.Wilkes in *Ionic Liquids in Synthesis*, *1st ed.* (Eds: P. Wasserscheid, T. Welton), Wiley-VCH: Weinheim, Germany, **2003**, p. 1.

[7] J. S. Wilkes, *J. Mol. Catal. A: Chem*. **2004**, *214*, 11.

[8] I. Krossing, J. M. Slattery, C. Daguenet, P. J. Dyson, A. Oleinikova, H. Weingärtner, *J. Am. Chem. Soc*. **2006**, *128*, 13427.

[9] H. Xue, R. Verma, J. M. Shreeve, *J. Fluorine Chem*. **2006**, *127*, 159.

[10] E. A. Turner, C. C. Pye, R. D. Singer, *J. Phy. Chem. A*. **2003**, *107,* 2277.

[11] R. S. Varma, V. V. Namboodiri, *Chem. Commun.* **2001**, 643.

[12] J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, R. D. Rogers, *Green Chem.* **2001**, *3*, 156.

[13] N. Winterton, *J. Matr. Chem.* **2001**, *16*, 4281.

[14] S. Park, R. J. Kazlauskas, *J. Org. Chem.* **2001**, *66*, 8395.

[15] F. van Rantwiijk, R. A. Sheldon, *Chem. Rev.* **2007**, *107*, 2757.

[16] V. I. Pârvulescu, C. Hardacre, *Chem. Rev.* **2007**, *107*, 2615.

[17] M. Haumann, A. Riisager, *Chem. Rev.* **2008**, *108,* 1474.

[18] M. A. P. Martins, C. P. Frizzo, D. N. Moreira, N. Zanatta, H. G. Bonacorso, *Chem. Rev.* **2008**, *108*, 2015.

[19] L. A. Blanchard, D. Hancu, E. J. Beckman, J. F. Brenecke, *Nature* **1999**, *399*, 28.

[20] N. Byrne, P. C. Howlett, D. R. MacFarlane, M. Forsyth, *Adv. Mater.* **2005**, *17*, 2497.

[21] P. Wang, S. M. Zakeeruddin, J.-E. Moser, M. Graetzel, *J. Phys. Chem. B* **2003**, *107*, 13280.

[22] N. Yamanaka, R. Kawano, W. Kubo, T. Kitamura, Y. Wada, M. Watanabe, S. Yanagida, *Chem*. *Commun*. **2005**, 740.

[23] P. Hapiot, C. Lagrost, *Chem. Rev.* **2008**, *108*, 2238.

[24] *Ionic Liquids: Industrial Applications for Green Chemistry, ACS Symp. Ser, Vol. 818*, (Eds: R. D. Rogers, K. R. Seddon), American Chemical Society, Washington DC, **2002**.

[25] M. J. Earle, K. R. Seddon, *Pure Appl. Chem*. **2000**, *72*, 1391.

[26] M. Freemantle, *Chem. Eng. News* **1998**, *76*, 32.

[27] A. J. Carmichael, M. Deetlefs. M. J. Earle, U. Fröhlich, K. R. Seddon in *Ionic Liquids as Green Solvents: Progress and Prospects, ACS Symp. Ser., Vol. 856*, (Eds: R. D. Rogers, K. R. Seddon), American Chemical Society, Washington DC, **2003**, pp.14-31.

[28] S. Gabriel, *Ber. Dtsch. Chem. Ges.* **1888**, *21*, 566.

[29] T. L. Cottrell, J. E. Gill, *J. Chem. Soc.* **1951**, 1798.

[30] P. Walden, *Bull. Acad. Sci. St. Petersburg* **1914**, 405.

[31] D. F. Evans, A. Yamauchi, R. Roman, E. Z. Casassa, *J. Colloid Interface Sci.* **1982**, *88*, 89.

[32] D. F. Evans, S.-H. Chen, G. W. Schriver, E. M. Arnett, *J. Am. Chem. Soc.***1981**, *103*, 481.

[33] D. F. Evans, A. Yamauchi, G. J. Wei, V. A. Bloomfield, *J. Phys. Chem. A* **1983**, *87*, 3537.

[34] J. S. Wilkes, J. A. Levisky, R. A. Wilson, C. L. Hussey, *Inorg. Chem.* **1982**, *21*, 1263.

[35] A. A. Fannin, D. A. Floreani, L. A. King, J. S. Landers, B. J. Piersma, D. J. Stech, R. L. Vaughn, J. S. Wilkes, W. L. John, *J. Phys. Chem.* **1984**, *88*, 2614.

[36] R. J. Gale, B. Gilbert, R. A. Osteryoung, *Inorg. Chem.* **1978**, *17*, 2728.

[37] Z. J. Karpinski, R. A. Osteryoung, *Inorg. Chem.* **1984,** *23*, 1491.

[38] S. Tait, R. A. Osteryoung, *Inorg. Chem.* **1984**, *23*, 4352.

[39] T. A. Zawodzinski, R. A. Osteryoung, *Inorg. Chem.* **1990**, *29*, 2842.

[40] R. A. Mantz, P. C. Trulove, R. T. Carlin, R. A. Osteryoung, *Inorg. Chem.* **1995**, *34*, 3846.

[41] J. S. Wilkes, M. J. Zaworotko, *Chem. Commun.* **1992**, *13*, 965.

[42] *Ionic Liquids in Synthesis*, 2nd ed. (Eds: P. Wasserscheid, T. Welton), Wiley-VCH: Weinheim, Germany, **2007**.

[43] K. R. Seddon, *J. Chem. Tech. Biotechnol.* **1997**, *68*, 351.

[44] H. L. Ngo, K. LeCompte, L. Hargens, A. B. McEwen, *Thermochim. Acta* **2000**, *357*, 97.

[45] A. Elaiwi, P. B. Hitchcock, K. R. Seddon, N. Srinivasan, Y.-M. Tan, T. Welton, J. A. Zora, *Inorg. Chem.* **1995**, *21*, 3467.

[46] S. Saha, S. Hayashi, A. Kobayashi, H. O. Hamaguchi, *Chem. Lett.* **2003**, *32*, 740.

[47] J. D. Holbrey, W. M. Reichert, M. Nieuwenhuyzen, S. Johnson, K. R. Seddon, R. D. Rogers, *Chem. Commun.* **2003**, *14*, 1636.

[48] J. D. Holbrey, K. R. Seddon, *Inorg. Chem.* **1999**, *13*, 2133.

[49] P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.* **1996***, 35*, 1168.

[50] D. Appleby, C. L. Hussey, K. R. Seddon, J. R. Turp, *Nature* **1986**, *323*, 614.

[51] J.-P. Belieres, C. A. Angell, *J. Phys. Chem. B* **2007**, *111*, 4926.

[52] M. J. Earle, J. M. S. S. Esperanca, M. A. Gilea, J. N. Canongia Lopes, L. P. N. Rebelo, J. W. Magee, K. R. Seddon, J. A. Widegren, *Nature* **2006***, 439*, 831.

[53] P. Wasserscheid, *Nature* **2006**, *439*, 797.

[54] M. Van Valkenburg, R. Vaughn, M. Williams, J. Wilkes, *Ionic Liquid Heat Transfer Fluids; paper presented at the 15th Symposium on Thermophysical Properties*, Boulder, Colorado, USA, 22-27 June **2003**.

[55] J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, R. D. Rogers, *Green Chem.* **2001**, *3*, 156.

[56] S. Takahashi, N. Koura, S. Kohara, M. L. Saboungi, L. A. Curtiss, *Plasmas & Ions* **1999**, *2*, 91.

[57] K. R. Seddon, A. Stark, M.-J. Torres, *Pure Appl. Chem.* **2000**, *72*, 2275.

[58] J. Jacquemin, P. Husson, A. A. H. Padua, V. Majer, *Green Chem.* **2006**, *8*, 172.

[59] E. I. Cooper, E. J. M. O´Sullivan, in: *Molten Salts*, *Electrochem. Soc. Proc. Ser., PV 92-16* (Eds: R. J. Gale, G. Blomgren, H. Kojima), Pennington, NJ, **1992**, p. 386.

[60] O. O. Okoturo, T. J. VanderNoot, *J. Electroanal. Chem*. **2004**, *568*, 167.

[61] K. R. Seddon, A. Stark, M.-J. Torres, in *Clean Solvents. Alternative Media for Chemical Reactions and Processing, ACS Symp. Ser., Vol. 819* (Eds: M. A. Abraham, L. Moens), Washigton DC, **2004**, pp. 34-49.

[62] K. R. Harris, M. Kanakubo, L. A. Woolf, *J. Chem. Eng. Data* **2007**, *52*, 1080.

[63] A. J. Carmichael, K. R. Seddon, *J. Phys. Org. Chem.* **2000**, *13*, 591.

[64] M. J. Muldoon, C. M. Gordon, I. R. Dunkin, *J. Chem. Soc., Perkin Trans. 2* **2001**, *4*, 433.

[65] C. Reichardt, *Green Chem.* **2005**, *7*, 339.

[66] T. L. Greaves, C. J. Drummond, *Chem. Rev.* **2008**, *108*, 206.

[67] J. L. Anderson, D. W. Armstrong, G.-T. Wei, *Anal. Chem.* **2006**, *78*, 2892.

[68] V. I. Parvulescu, C. Hardacre, *Chem. Rev.* **2007**, *107*, 2615.

[69] A. Stark, B. L. MacLean, R. D. Singer, *J. Chem. Soc., Dalton Trans.* **1999**, 63.

[70] B. C. Ranu, S. Banerjee, R. Jana, *Tetrahedron* **2007**, *63*, 776.

[71] N. Ranpoor, H. Firouzabadi, R. Azadi, *Tetrahedron Lett.* **2006**, *47*, 5531.

[71] B. M. Khadilkar, G. L. Rebeiro, *Org. Process Res. Dev.* **2002**, *6*, 826.

[73] K. Fukumoto, H. Ohno, *Angew. Chem. Int. Ed.* **2007**, *46*, 1852.

[74] I. Krossing, J. M. Slattery, P. J. Dyson, A. Oleinikova, H. Weingärtner, *J. Am. Chem. Soc.* **2006**, *128*, 13427.

[75] L. A. Blanchard, D. Hancu, E. J. Beckman, J. F. Brenecke, *Nature* **1999**, *399*, 28.

[76] C. Wakai, A. Oleinikova, M. Ott, H. Weingärtner, *J. Phys. Chem. B* **2005**, *109*, 17028.

[77] A. Beyaz, W. S. Oh, V. P. Reddy, *Coll. Surf. B: Biointerfaces* **2004**, *35*, 119.

[78] R. P. Swatloski, S. K. Spear, J. D. Holbrey, R. D. Rogers, *J. Am. Chem. Soc.* **2002**, *124*, 4974.

[79] O. El Seoud, A. Koschella, L. C. Fidale, S. Dorn, T. Heinze, *Biomacromolecules* **2007**, *8*, 2629.

[80] M. Gericke, K. Schlufter, T. Liebert, T. Heinze, T. Budtova, *Biomacromolecules* **2009**, *10*, 1188.

[81] S. Seki, Y. Kobayashi, H. Miyashiro, Y. Ohno, A. Usami, Y. Mita, M. Watanabe, N. Terada, *Chem. Commun.* **2006**, *5*, 544.

[82] F. Endres, *Nachrichten aus der Chemie* **2007**, *55*, 507.

[83] W. Yang, H. Cang, Y. Tang, J. Wang, Y. Shi, *J. Appl. Electrochem.* **2008**, *38*, 537.

[84] Y. Cao, J. Zhang, Y. U. Bai, R. Li, S. M. Zakeeruddin, M. Gratzel, P. Wang, *J. Phys. Chem. C* **2008**, *112*, 13775.

[85] D. Kuang, S. Uchida, R. Humphry-Baker, S. M. Zakeeruddin, M. Graetzel, *Angew. Chem Int. Ed.* **2008**, *47*, 1923.

[86] P. Wang, S. M. Zakeeruddin, J.-E. Moser, M. Graetzel, *J. Phys. Chem. B* **2003**, *107*, 13280.

[87] N. Yamanaka, R. Kawano, W. Kubo, T. Kitamura, Y. Wada, M. Watanabe, S. Yanagida, *Chem. Commun*. **2005**, 740.

[88] B. Weyershausen, K. Hell, U. Hesse, *Green Chem.* **2005**, *7*, 283.

[89] G. Buehler, C. Feldman, *Angew. Chem. Int. Ed.* **2006**, *45*, 4864.

[90] C. J. Adams, A. E. Bradley, K. R. Seddon, *Aust. J. Chem.* **2001**, *54*, 679.

[91] Y. Zhou, M. Antonietti, *Adv. Mater.* **2003**, *15*, 1452.

[92] L. Yang, W. Meijia, L. I. Zhiying, L. Hongtao, H. E. Ping, L. I. Jinghong, *Langmuir* **2005**, *21*, 1618.

[93] L. I. Zhonghao, L. Zhimin, Z. Jianling, H. Buxing, D. U. Jimin, G. Yanan, *J. Phys. Chem. B* **2005**, *109*, 14445.

[94] H. Kaper, F. Endres, I. Djerdj, M. Antonietti, B. Smarsly, J. Maier, Y.-S. Hu, *Small* **2007**, *3*, 1753.

[95] T. Wang, H. Kaper, M. Antonietti, B. Smarsly, *Langmuir* **2007**, *23*, 1489.

[96] E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald, R. E. Morris, *Nature* **2004**, *430*, 1012.

[97] N. Doerr, E. Kenesey, C. Oetsch, A. Ecker, A. Pauschitz, F. Franek, *Tribology and Interface Engineering Series* **2005**, *48*, 123.

[98] N. Canter, *Tribology & Lubrication Technology* **2007**, *63*, 12.

[99] M. Maase, K. Massonne, K. Halbritter, R. Noe, M. Bartsch, W. Siegel, V. Stegmann, M. Flores, O. Huttenloch, M. Becker, *Method for the separation of acids from chemical reaction mixtures by means of ionic fluids*, BASF AG, Patent WO 2003062171, **2003**.

[100] V. Stegmann, K. Massonne, *Method for producing haloalkanes from alcohols,* BASF AG, Patent WO 2005026089, **2005**.

[101] H. Zhang, K. Hong, J. W. Mays, *Macromolecules* **2002**, *35*, 5738.

[102] T. Sarbu, K. Matyjaszewski, *Macromol. Chem. Phys.* **2001**, *202*, 3379.

[103] S. Ding, M. Radosz, Y. Shen, *Macromolecules* **2005**, *38*, 5921.

[104] Y. Shen, S. Ding, *Prog. Polym. Sci.* **2004**, *29*, 1053.

[105] T. Biedron, P. Kubisa, *Polym. Int.* **2003**, *52*, 1584.

[106] T. Biedron, P. Kubisa, *J. Polym. Sci. Part A, Polym. Chem.* **2002**, *40*, 2799.

[107] T. Biedron, P. Kubisa, *Macromol. Rapid Commun.* **2001**, *22*, 1237.

[108] S. Perrier, T. P. Davis, A. J. Carmichael, D. M. Haddleton, *Chem. Commun.* **2002**, 2226.

[109] J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, L. Jeffery, R. T. A. Mayadunne, *Macromolecules* **1998**, *31*, 5559.

[110] R. Vijayaraghavan, D. R. MacFarlane, *Chem. Commun.* **2004**, 700.

[111] P. Kubisa, *Prog. Polym. Sci.* **2004**, *29*, 3.

[112] H. Ohno, *Macromol. Symp.* **2007**, *249*, 551.

[113] M. Hirao, K. Ito, H. Ohno, *Electrochim. Acta.* **2000**, *45*, 1291.

[114] H. Ohno, K. Ito, *Chem. Lett.* **1998**, 751.

[115] M. Yoshizawa, W. Ogihara, H. Ohno, *Polym. Adv. Technol.* **2002**, *13*, 589.

[116] M. Yoshizawa, M. Hirao, K. Ito, H. Ohno, *Mater. Chem.* **2001**, *11*, 1057.

[117] W. Ogihara, S. Washiro, H. Nakajima, H. Ohno, *Electrochim. Acta* **2006**, *51*, 2614.

[118] H. Nakajima, H. Ohno, *Polymer* **2005**, *46*, 11499.

[119] M. J. Muldoon, C. M. Gordon, *J. Polym. Sci. Part A, Polym. Chem.* **2004**, *42*, 3865.

[120] H. L. Ricks-Laskoski, A. W. Snow, *J. Am. Chem. Soc.* **2006**, *128*, 12402.

[121] F. Yan, J. Texter, *Chem. Commun.* **2006**, 2696.

[122] F. Yan, J. Texter, *Angew. Chem. Int. Ed.* **2007**, *46*, 2440.

[123] S. Amajjahe, H. Ritter, *Macromolecules* **2008,** *41,* 716.

[124] S. Amajjahe, H. Ritter, *Macromolecules* **2008**, *41*, 3250.

[125] J.-M. Lehn, *Proc. Nat. Acad. Sci. USA* **2002**, *99*, 4763.

[126] F. Vögtle, *Supramolecular Chemistry: An Introduction*, Wiley, New York, **1991**.

[127] J.-M. Lehn, *Supramolecular Chemistry. Concepts and Perspectives*, VCH, Weinheim, **1995**.

[128] *Comprehensive Supramolecular Chemistry*, *Vol 1-11* (Eds: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle), Pergamon Press, Oxford, **1996**.

[129] J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, Wiley, New York, **2000**.

[130] H.-J. Schneider, A. Yatsimirsky, *Principles and Methods in Supramolecular Chemistry*, Wiley, New York, **2000**.

[131] E. L. Shakhnovich, V. Abkevich, O. Ptitsyn, *Nature* **1996**, *379*, 96.

[132] A. Klug, *Angew. Chem. Int. Ed.* **1983**, *22*, 565.

[133] E. Fischer, *Ber. Dtsch. Chem. Ges.* **1894,** *27*, 2985.

[134] D. J. Cram, J. M. Cram, *Science* **1974**, *183*, 803.

[135] B. Dietrich, J.-M. Lehn, J.-P. Sauvage, *Tetrahedron Lett*. **1969**, *10*, 2889.

[136] B. Dietrich, J.-M. Lehn, J.-P. Sauvage, J. Blanzat, *Tetrahedron* **1973**, *29*, 1629.

[137] B. Dietrich, J.-M. Lehn, J.-P. Sauvage, *Tetrahedron* **1973**, *29*, 1647.

[138] J.-M. Lehn, *Struct. Bonding* **1973**, *16*, 1.

[139] C. J. Pedersen, *J. Am. Chem. Soc.* **1967**, *89*, 7017.

[140] C. J. Pedersen, *Angew. Chem. Int. Ed.* **1988**, *27*, 1053.

[141] J.-M. Lehn, M. Mascal, A. Decian, J. Fischer, *J. Chem. Soc. Chem. Comm.* **1990**, *6*, 479.

[142] J.-M. Lehn, M. Mascal, A. Decian, J. Fischer, *J. Chem. Soc., Perkin Trans. 2* **1992**, *4*, 461.

[143] N. Zimmerman, J. S. Moore, S. C. Zimmerman, *Chem. Ind.* **1998**, *15*, 604.

[144] J. S. Moore, *Curr. Opin. Colloid Interface Sci.* **1992**, *4*, 108.

[145] L. Brunsveld, B. J. B. Folmer, E. W. Meijer, R. P. Sijbesma, *Chem. Rev.* **2001**, *101*, 4071.

[146] *Supramolecular polymers*. 2nd ed (Ed: A. Ciferri), CRC Press: Taylor and Francis: Boca Raton, FL, **2005**.

[147] V. T. D'Souza, K. B. Lipkowitz, *Chem. Rev.* **1998**, *98*, 1741.

[148] A. F. D. de Namor, R. M. Cleverley, M. L. Zapata-Ormachea, *Chem. Rev.* **1998**, *98*, 2495.

[159] L. Baldini, A. Casnati, F. Sansone, R. Ungaro, *Chem. Soc. Rev.* **2007**, *36*, 254.

[150] J. S. Kim, D. T. Quang, *Chem. Rev.* **2007**, *107*, 3780.

[151] K. Kim, N. Selvapalam, D. H. Oh, *J. Incl. Phenom. Macrocycl. Chem.* **2004**, *50*, 31.

[152] J. Lagona, P. Mukhopadhyay, S. Chakrabarti, L. Isaacs, *Angew. Chem. Int. Ed.* **2005**, *44*, 4844.

[153] K. Kim, N. Selvapalam, Y. H. Ko, K. M. Park, D. Kim, J. Kim, *Chem. Soc. Rev.* **2007**, *36*, 267.

[154] K. Skopek, M. C. Hershberger, J. A. Gladysz, *Coord. Chem. Rev.* **2007**, *251*, 1723.

[155] K. E. Krakowiak, J. S. Bradshaw, H. An, R. M. Izatt, *Pure Appl. Chem.* **1993**, *65*, 511.

[156] P. D. W. Boyd, C. A. Reed, *Acc. Chem. Res.* **2005**, *38*, 235.

[157] K. Tashiro, T. Aida, *Chem. Soc. Rev.* **2007**, *36*, 189.

[158] F. M. Raymo, *Angew. Chem. Int. Ed.* **2006**, *45*, 5249.

[159] G. V. Oshovsky, D. N. Reinhoudt, W. Verboom, *Angew. Chem. Int. Ed.* **2007**, *46*, 2366.

[160] J. Rebek, *Angew. Chem. Int. Ed.* **1990**, *29*, 245.

[161] D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2715.

[162] M. C. T. Fyfe, J. F. Stoddart, *Acc. Chem. Res.* **1997**, *30*, 393.

[163] A. Harada, J. Li, M. Kamachi, *Nature* **1992**, *356*, 325.

[164] A. Harada, J. Li, M. Kamachi, *Nature* **1994**, *370*, 126.

[165] K. Hirose, *J. Incl. Phenom. Macrocycl. Chem.* **2001**, *39*, 193.

[166] A. Villiers, *Rend Acad. Sci.* **1891**, *112*, 536.

[167] F. Schardinger, *Wien Klin. Wochenschr.* **1904**, *17*, 207.

[168] K. Freudenberg, M. Meyer-Delius, *Ber. Dtsch. Chem. Ges.* **1938**, *71*, 1596.

[169] K. Freudenberg, F. Cramer, H. Plieninger, *Verfahren zur Herstellung von Einschluss-verbindungen physiologisch wirksamer organischer Verbindungen*, Knoll AG Chemische Fabriken, German Patent No. 895, 769, **1953**.

[170] M. L. Bender, M. Komiyama, *Cyclodextrin chemistry*, Springer Verlag, Berlin **1978**.

[171] J. A. Thoma, L. Steward, in *Starch: chemistry and technology*, 1th ed. (Eds: R. L. Whistler, E. F. Paschall), Academic Press, New York (US), **1965**, pp. 209-249.

[172] F. R. Senti, S. R. Erlander, in *Non-stoichiometric compounds* (Ed: L. Mandelcorn), Academic Press, New York (US), **1964**, p. 588.

[173] F. Cramer, H. Hettler, *Naturwiss.* **1967**, *54*, 625.

[174] M. L. Bender, M. Komiyama, in *Bioorganic chemistry*, *Vol 1* (Ed: E. E. van Tamelen), Academic Press, New York (US), **1977**, Chap. 2, pp. 19-57.

[175] V. Schurig, H.-P. Nowotny, *Angew. Chem.* **1990**, *102*, 969; *Angew. Chem. Int. Ed.* **1990**, *29*, 939.

[176] M. E. Brewster, T. Loftsson, *Adv. Drug Deliv. Rev.* **2007**, *30*, 645.

[l77] A. Maciollek, M. Munteanu, H. Ritter, *Macromol. Chem. Phys.* **2010**, *211*, 245.

[178] L. Szente, J. Szejtli, *Trends Food Sci. Technol.* **2004**, *15*, 137.

[179] G. Cravotto, A. Binello, E. Baranelli, P. Carraro, F. Trotta, *Curr. Nutr. Food Sci.* **2006**, *2*, 343.

[180] G. Astray, C. Gonzalez-Barreiro, J. C. Mejuto, R. Rial-Otero, J. Simal-Gándara, *Food Hydrocoll.* **2009**, *23*, 1631.

[181] K. C. Caroll, M. L. Brusseau, *J. Contam. Hydrol.* **2009**, *106*, 62.

[182] L. Lorna Barr, P. Dumanski, C. Easton, J. Harper, K. Lee, S. Lincoln, A. Meyer, J. Simpson, *J. Incl. Phenom. Macrocycl. Chem.* **2004**, *50*, 19.

[183] St. Bernhardt, P. Glöckner, A. Theis, H. Ritter, *Macromolecules* **2001**, *34*, 1647.

[184] T. Ogoshi, A. Harada, *Sensors* **2008**, *8*, 4961.

[185] C. Koopmans, H. Ritter, *J. Am. Chem. Soc.* **2007**, *129*, 3502.

[186] D. French, *Adv. Carbohydrate Chem.* **1957**, *12*, 189.

[187] W. Saenger, *Angew. Chem. Int. Ed.* **1980**, *19*, 344; *Angew. Chem.* **1980**, *92*, 343.

[188] D. French, A. O. Pulley, J. A. Effenberger, M. A. Rougvie, M. Abdullah, Arch. Biochem. Biophys. **1965**, *111*, 153.

[189] H. Ueda, T. Endo, in *Cyclodextrins and Their Complexes*, 1th ed. (Ed: H. Dodzink), Wiley-VCH: Weinheim, Germany, **2006**, pp. 370-380.

[190] I. Tabushi, *Acc. Chem. Res.* **1982**, *15*, 66.

[191] S. Anderson, T. D. W. Claridge, H. L. Anderson, *Angew. Chem. Int. Ed.* **1997**, *36*, 1310.

[192] K. A. Connors, *Chem. Rev.* **1997**, *97*, 1325.

[193] M. V. Rekharsky, Y. Inoue, *Chem. Rev.* **1998**, *98*, 1875.

[194] *Cyclodextrin Technology*, 1th ed. (Ed: J. Szejtli), Springer, New York (US), **1988**.

[195] *Comprehensive Supramolecular Chemistry: Cyclodextrins, Vol 3* (Eds: J. Szejtli, T. Osa), Permagon, Oxford, **1996**.

[196] J. Solms, R. H. Egli, *Helv. Chim. Acta* **1965**, *48*, 1225.

[197] E. Renard, A. Deratani, G. Volet, B. Sébille, *Eur. Poly. J.* **1997**, *33*, 49.

[198] M. Furue, A. Harada, S. Nozakura, *J. Polym. Sci., Polym. Lett.* **1975**, *13*, 357.

[199] A. Harada, M. Furue, S. Nozakura, *Macromolecules* **1976**, *9*, 701.

[200] A. Harada, M. Furue, S. Nozakura, *Macromolecules* **1976**, *9*, 705.

[201] M. Munteanu, S. Choi, H. Ritter, *Macromolecules* **2008**, 41, 9619.

[202] M. Weickenmeier, G. Wenz, *Macromol. Rapid. Commun.* **1996**, *17*, 731.

[203] J. Szejtli, *Stärke* **1984**, *36*, 429.

[204] I. Tomatsu, A. Hashidzume, A. Harada, *Macromolecules* **2005**, *38*, 5223.

[205] Y. Ohya, S. Takamido, K. Nagahama, T. Ouchi, R. Katoono, N. Yui, *Macromolecules* **2009**, *10*, 2261.

[206] G. Wenz, B. H. Han, A. Müller, *Chem. Rev.* **2006**, *106*, 782.

[207] M. Born, H. Ritter, *Angew. Chem* **1995**, *107*, 342; *Angew. Chem. Int. Ed.* **1995**, *34*, 309.

[208] O. Noll, H. Ritter, *Macromol. Rapid Commun.* **1997**, *18*, 53.

[209] M. Munteanu, S. Choi, H. Ritter, *J. Incl. Phenom. Macrocycl. Chem.* **2008**, *62*, 197.

[210] J. E. Moses, A. D. Moorhouse, *Chem. Soc. Rev.* **2007**, *36*, 1249.

[211] H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2001**, *40*, 2004.

[212] P. Lundberg, C. J. Hawker, A. Hult, M. Malkoch, *Macromol. Rapid Commun.* **2008**, *29*, 998.

[213] A. Michael, *J. Prakt. Chem.* **1893**, *48*, 94.

[214] R. Huisgen, *Angew. Chem. Int. Ed.* **1963**, *2*, 565.

[215] R. Huisgen, *Angew. Chem. Int. Ed.* **1963**, *2*, 633.

[216] J. E. Moses, A. D. Moorhouse, *Chem. Soc. Rev*. **2007**, *36*, 1249.

[217] C. W. Tornøe, C. Christensen, M. Meldal, *J. Org. Chem.* **2002**, *67*, 3057.

[218] V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2002**, *41*, 2596.

[219] P. Appukkuttan, W. Dehaen, V. V. Fokin, E. Van der Eycken, *Org. Lett.* **2004**, *6*, 4223.

[220] Y. L. Angell, K. Burgess, *Chem. Soc. Rev.* **2007**, *36*, 1674.

[221] H. Binder, C. Kluger, *Curr. Org. Chem.* **2006**, *10*, 1791.

[222] V. D. Bock, H. Hiemstra, J. H. van Maarseveen, *Eur. J. Org. Chem.* **2006**, 51.

[223] A. Dondoni, *Chem. Asian J.* **2007**, *2*, 700.

[224] J.-F. Lutz, *Angew. Chem. Int. Ed.* **2007**, *46*, 1018.

[225] W. D. Sharpless, P. Wu, T. V. Hansen, J. G. Lindberg, *J. Chem. Educ.* **2005**, *82*, 1833.

[226] P. Wu, V. V. Fokin, *Aldrich Chim. Acta* **2007**, *40*, 7.

[227] J. P. Collman, N. K. Devaraj, C. E. D. Chidsey, *Langmuir* **2004**, *20*, 1051.

[228] D. D. Díaz, S. Punna, P. Holzer, A. K. McPherson, K. B. Sharpless, V. V. Fokin, M. G. Finn, *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 4392.

[229] B. Helms, J. L. Mynar, C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2004**, *126*, 15020.

[230] J.-F. Lutz, H. G. Börner, K. Weichenhan, *Macromol. Rapid Commun.* **2005**, *26*, 514.

[231] P. Wu, A. K. Feldman, A. K. Nugent, C. J. Hawker, A. Scheel, B. Voit, J. Pyun, J. M. J. Frechet, K. B. Sharpless, V. V. Fokin, *Angew. Chem. Int. Ed.* **2004**, *43*, 3928; Angew. Chem. **2004**, *116*, 3915.

[232] M. Meldal, *Macromol. Rapid Commun.* **2008**, *29*, 1016.

[233] V. O. Rodionov, V. V. Fokin, M. G. Finn, *Angew. Chem. Int. Ed.* **2005**, *44*, 2210.

[234] S. Punna, J. Kuzelka, Q. Wang, M. G. Finn, *Angew. Chem. Int. Ed.* **2005**, *44*, 2215.

[235] H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2001**, *40*, 2004.

[236] C. J. Hawker, K. L.Wooley, *Science* **2005**, *309*, 1200.

[237] W. H. Binder, R. Sachsenhofer, *Macromol. Rapid Commun.* **2007**, *28*, 15.

[238] S. Svenson, D. A. Tomalia, *Adv. Drug Delivery Rev.* **2005**, *57*, 2106.

[239] B. Voit, *New J. Chem.* **2007**, *31*, 1139.

[240] H. Nandivada, X. Jiang, J. Lahann, *Adv. Mater.* **2007**, *19*, 2197.

[241] G. W. Goodall, W. Hayes, *Chem. Soc. Rev.* **2006**, *35*, 280.

[242] R. A. Evans, *Aust. J. Chem.* **2007**, *60*, 384.

[243] W. H. Binder, R. Sachsenhofer, *Macromol. Rapid Commun.* **2008**, *29*, 952.

[244] D. Fournier, R. Hoogenboom, U. S. Schubert, *Chem. Soc. Rev.* **2007**, *36*, 1369.

[245] Special Issue: *Click Chemistry in Polymer Science* (Eds: W. H. Binder), *Macromol. Rapid Commun*. **2008**, 12-13, pp. 943-1185 and *Aust. J. Chem.* **2007**, 60, pp. 381-444.

[246] S. Choi, M. Munteanu, H. Ritter, *J. Polym. Res.* **2009**, *16*, 389.

[247] S. Amajjahe, S. Choi, M. Munteanu, H. Ritter, *Angew. Chem. Int. Ed.* **2008**, *47*, 3435.

[248] J. Xu, S. Liu, *J. Polym. Sci, Part A: Polym. Chem.* **2009**, *47*, 404.

[249] J. Wu, H. He, C. Gao, *Macromolecules* **2010**, *43*, 2252.

[250] A. Méndez-Ardoy, M. Gómez-García, C. Ortiz Mellet, N. Sevillano, M. D.s Girón, R. Salto, F. Santoyo-González, J. M. García Fernández, *Org. Biomol. Chem.* **2009**, *7*, 2681.

[251] T. Liebert, C. Hänsch, T. Heinze, *Macromol. Rapid Commun.* **2006**, *27*, 208.

[252] T. Hasegawa, M. Umeda, M. Numata, C. Li, A.-H. Bae, T. Fujisawa, S. Haraguchi, K. Sakuraib, S. Shinkai, *Carbohydr. Res.* **2006**, *341*, 35.

[253] J. Hafrén, W. Zou, A. Córdova, *Macromol. Rapid Commun.* **2006**, *27*, 1362.

[254] T. Heinze, M. Schöbitz, M. Pohl, F. Meister, *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3853.

[255] A. Koschella, M. Richter, T. Heinze, *Carbohydr. Res.* **2010**, *345*, 1028.

[256] Y. Gao, Z. Zhang, L. Chen, W. Gu, Y. Li, *Biomacromolecules* **2009**, *10*, 2175.

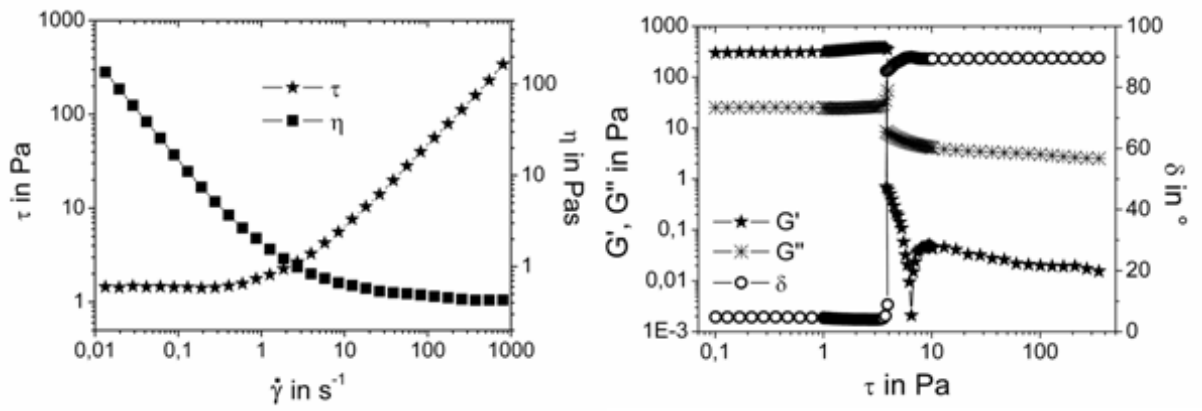
[257] I. Filpponen, D. S. Argyropoulos, *Biomacromolecules* **2010,** *11,* 1060.

[258] J. Zhang, X.-D. Xu, D.-Q. Wu, X.-Z. Zhang, R.-X. Zhuo, *Carbohydr. Polym.* **2009**, *77*, 583.

[259] V. Crescenzi, L. Cornelio, C. DiMeo, S. Nardecchia, R. Lamanna, *Biomacromolecules* **2007**, *8*, 1844.

Chapter 2

Rheological Behavior of Cyclodextrin Dissolved in Ionic Liquids



Abstract

The rheology of solutions of randomly methylated (1.8) β-cyclodextrin (m-β-CD) in 1-ethyl-3-methyl imidazolium acetate [EMIM][Ac] was studied in detail by rotational and oscillatory shear measurements. It was found that a gel structure was formed even at a relatively low m-β-CD concentration, which induced intriguing results in oscillation experiments. The solutions showed abrupt changes of the structurally dependent rheological moduli and reproducible transitions from gel to sol state at specific shear stress. For all m-β-CD solutions a non-Newtonian flow behavior including shear thinning was obtained and analyzed with the Bingham model. The influence of temperature and m-β-CD concentration on the flow behavior was studied for all solutions, and the flow activation energies were calculated from the logarithmic form of the Arrhenius equation for non-associating electrolytes.

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2 Rheological Behavior of Cyclodextrin Dissolved in Ionic Liquids

2.1 Introduction

Cyclodextrins (CDs) are cyclic oligoamyloses based on α-1,4-linked D-glucose units. Due to their conical, tubelike shape, CDs are able to enclose suitable hydrophobic molecules reversibly.[1-3] In the last decade, a large number of applications in pharmaceutical and analytical chemistry, food technology, chemical synthesis, and catalysis have been developed.[4,5]

As a new type of "green solvent", ionic liquids (ILs) are currently in the focus of increasing scientific interest. Their distinguished physical properties, such as excellent thermal stability, negligible vapor pressure, high electrical conductivity and the usage as a special solvent, open a broad field of applications. This includes the improved solubility of cellulose and CDs in ILs.[6-12] Since the interaction between ILs and CDs plays a crucial role in analytical chemistry and material synthesis,[13-15] the understanding of the rheological properties of CD/IL solutions is an important prerequisite for a successful processing. A survey of the relevant literature reveals that no further investigations on the rheological behavior of CD dissolved in IL have been made.

In the following, a comprehensive investigation on the rheological properties of randomly methylated (1.8) β-cyclodextrin (m-β-CD) / 1-ethyl-3-methyl imidazolium acetate [EMIM][Ac] solutions is presented, including oscillatory and rotational shear experiments as well as the influence of temperature. m-β-CD concentrations were varied in a wide range from dilute (5 wt%) to an almost saturated state (25 wt%). Furthermore, some rheological data of [EMIM][Ac] are shown for comparison.

2.2 Results and Discussion

2.2.1 Dissolution Process

The dissolution behavior of randomly methylated (1.8) β-cyclodextrin (m-β-CD) in [EMIM][Ac] at different weight percentages was investigated. Since the change of electrostatic interactions and the formation of ordered structure of an ionic liquid (IL) dominates the ability to dissolve β-CD,[16] [EMIM][Ac] should be the appropriate solvent, because of its

weak anion/cation interactions. It was found that [EMIM][Ac] dissolves m-β-CD up to 25 wt% at room temperature to obtain transparent and viscous solutions. Solutions of lower concentrations, e.g. 5 wt% m-β-CD could be obtained in minutes, whereas the dissolution of 25 wt% m-β-CD in [EMIM][Ac] took several hours.

Because of the high degree of crystallinity of m-β-CD, the dissolution process in the isotropic IL could be observed by polarized light microscopy (PLM) as shown in Figure 2.1. In the undissolved state, the coronas of widespread crystals of chiral m-β-CD units were observed.

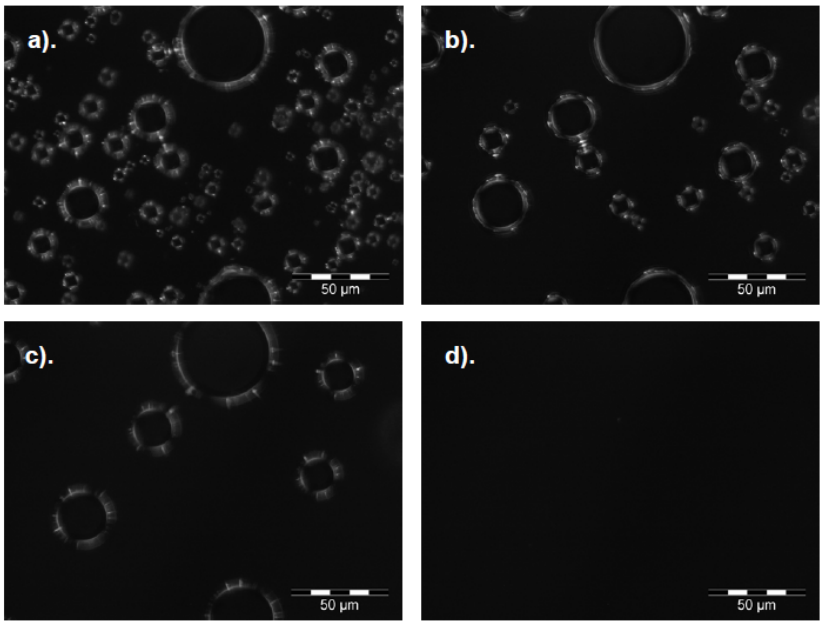


Figure 2.1 PLM images of the chronological sequence of m-β-CD (5 wt%) dissolution in [EMIM][Ac]; a) t = 0 min, b) t = 15 min, c) t = 45 min, d) t = 90 min.

2.2.2 Oscillatory measurements

Prior to the dynamic rheological measurements, amplitude sweeps were recorded with a constant frequency of 1 Hz and a shear stress varying from 0.1 to 300 Pa for all m-β-CD/[EMIM][Ac]-solutions. The weight percentages of β-CD in [EMIM][Ac] were between 5 and 25 wt%. In Figure 2.2, storage modulus G', loss modulus G'' and phase shift angle δ of a 15 wt% solution are shown exemplarily. Since G' > G'' at low shear stress, the system turns out to be a soft solid gel. A linear viscoelastic (LVE) plateau was observed up to 1% of strain,

where the initial gel structure broke, resulting in a sharp transition. δ shifted from 5° to 90° by only a slight change of shear stress of 0.2 Pa. Thus, the system shows an astonishingly abrupt change from almost ideal elastic to an ideal viscous behavior. At higher shear stress, G" outweighed G'.

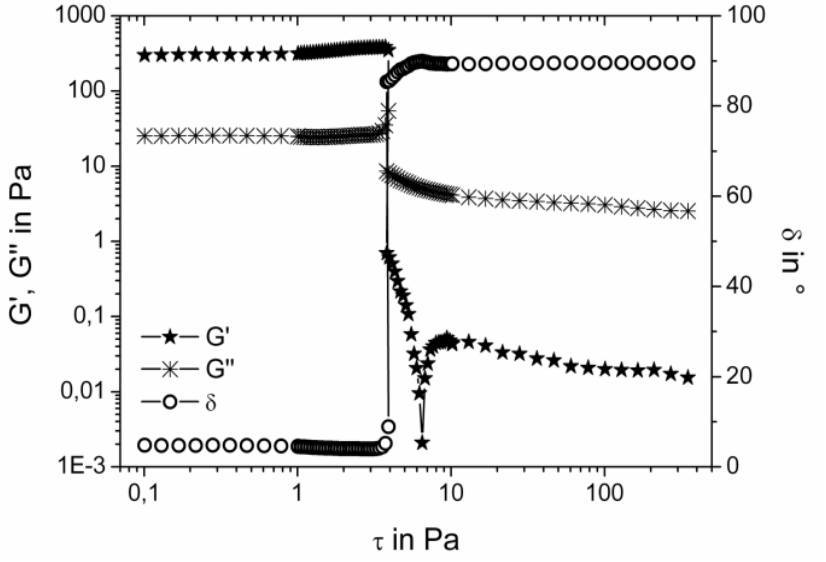


Figure 2.2 Amplitude sweep results for a solution of 15 wt% m-β-CD in [EMIM][Ac] at 23 °C.

As Figure 2.3 implies, the corresponding plot of the frequency sweep proves the gel structure of the system as G' and G" occurred in parallel straight lines throughout the entire frequency range. The values for G' were at least one decade higher than those for G". Thus, the system behaves like a rigid gel with a high degree of physical cross-linking, for example, energetic interactions. The shape of the curves is comparable to that indicated by cross-linked polymers, since both structures show a structural network. In contrast to that, frequency sweeps at a higher shear stress values, e.g., 100 Pa, showed a typical sol behavior with G" > G' and a constant phase shift angle δ of 90°.

To verify the reproducibility of this uncommon abrupt gel-sol transition, multiple cycles of amplitude sweeps were measured between 0.1 and 300 Pa (Figure 2.4). For all cycles, the three-dimensional network structure collapsed at a shear stress of 3.96 ± 0.1 Pa, whereas the gel structure was rebuilt immediately when the shear stress reached lower values (1.82 ± 0.01

Pa). Since the cycles were measured without a recovery phase, the small hysteresis provides evidence for pure shear thinning behavior and excludes thixotropy.

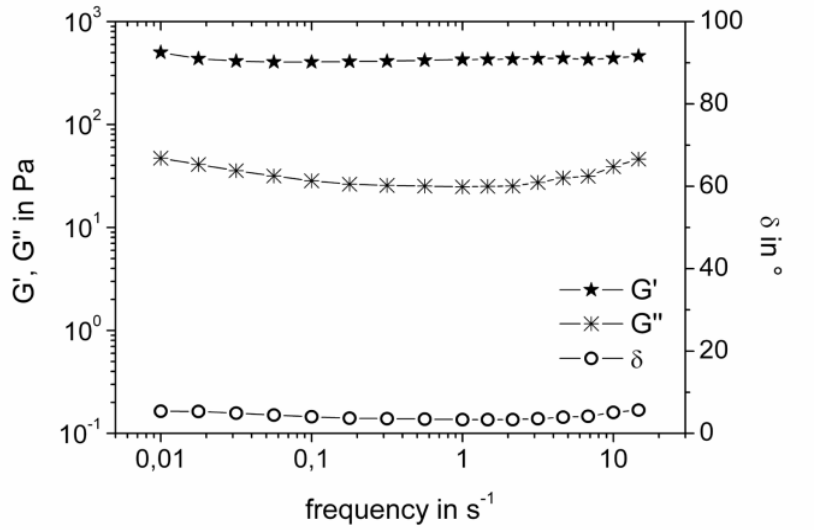


Figure 2.3 Storage modulus G', loss modulus G'' and phase shift angle δ as functions of the frequency f, exemplary for a 15 wt% solution at a shear stress of 0.5 Pa.

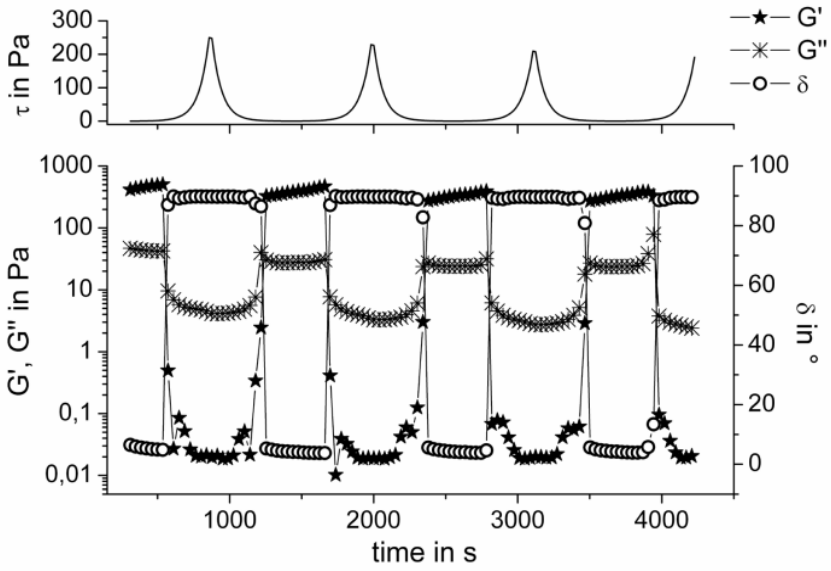


Figure 2.4 Cycles of amplitude sweeps for a 15 wt% m-β-CD/[EMIM][Ac] solution at 23 °C.

The abrupt gel-sol transition was achieved for all m-β-CD/[EMIM][Ac] solutions with increasing shear stress τ. The yield point τ_0 (G' = G") in dependency on the weight percentage of m-β-CD is shown in Figure 2.5. With increasing amounts of m-β-CD, a larger number of cross-linking points and, therefore, a denser physical interconnected gel structure was obtained. An approximated linear correlation was found.

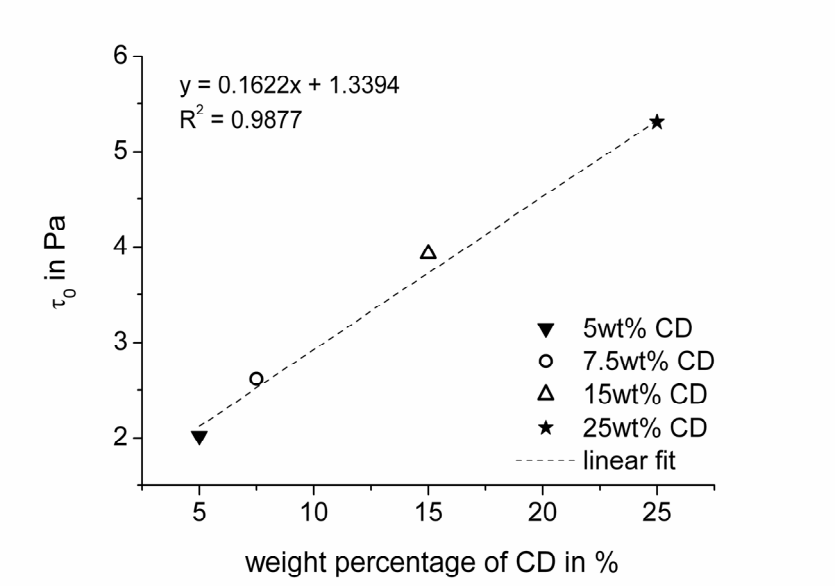


Figure **2.5** Yield point τ_0 as a function of m-β-CD weight percentage.

2.2.3 Rotational Measurements

The flow curves for the shear stress dependency of the shear rate Á for various m-β-CD/[EMIM][Ac] solutions are shown in Figure 2.6. For a better comparison, the rheological behavior of pure [EMIM][Ac] was evaluated as well. The recorded flow curves can be described by the Bingham equation (Eq. 1),

$$\tau = \tau_B + \eta_B \cdot Á \qquad (1)$$

where τ_B is the Bingham yield point and η_B is the so called Bingham flow coefficient for a given shear rate Á. The experimental results obtained, were fitted with the Bingham plot and the parameters are listed in Table 2.1.

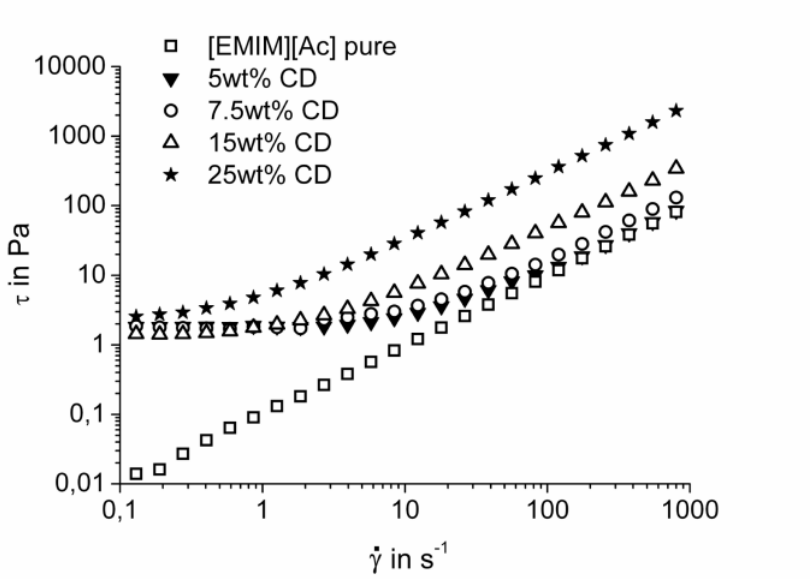


Figure 2.6 Flow curves of different m-β-CD/[EMIM][Ac] solutions at 23 °C.

Table 2.1 Parameters of the Bingham plot for β-CD/[EMIM][Ac]-solutions at 23 °C.

wt% m-β-CD	τ_B [Pa]	η_B [mPas]	R^2
5	1.86	102.8	0.9802
7.5	2.04	160.5	0.9949
15	2.29	424.6	0.9942
25	3.97	2899	0.9937

In figure 7, the corresponding viscosity curves are depicted. For all m-β-CD solutions, the viscosity decreased with increasing shear rates over 3-4 decades, before η became constant, which is typical for shear-thinning substances. Such a shear-thinning behavior derived from the degradation of the physical networks by increasing shear force until the viscosity shows a nearly Newtonian behavior. In the literature, it has already been described that dispersions of hematite in [C_2MIM][$EtSO_4$], hydrophobic silica nanoparticles in [BF_4] anion-based ILs, and dispersions of single-walled carbon nanotubes (SWCNTs) in [C_4mim][BF_4] show a similar shear-thinning behavior.[17-19] Furthermore, it was found that with increasing m-β-CD weight

percentages the plateau viscosities reached higher values. In contrast, viscosity curves of pure [EMIM][Ac] showed Newtonian behavior over the whole range of shear rates (0.01 s^{-1} - 1000 s^{-1}).[20]

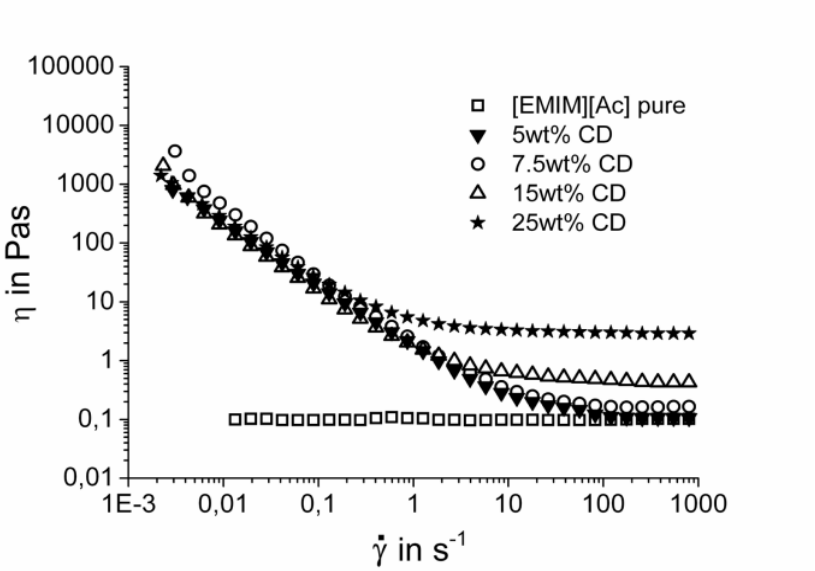


Figure 2.7 Viscosity curves of various m-β-CD/[EMIM][Ac] solutions in comparison to the applied shear rate at 23 °C.

Since no Newtonian plateau was obtained at lower shear rate values, even at 0.002 inverse seconds, the longest relaxation time was at least 500 seconds. Using the Debye-Stokes-Einstein equation (Eq. 2),[21]

$$\tau_r = \frac{4\pi r^3 \eta}{kT} \tag{2}$$

where r is the molecular radius, τ_r is the relaxation time, η is the viscosity of the solvent (93 mPas at 25 °C) and k is the Boltzmann constant, a minimum cluster size would be approximately 1200 nm. The calculated size is a further indication for the three-dimensional physical network existing in m-β-CD/[EMIM][Ac] solutions, since single m-β-CD molecules only have a size of 1 nm.[22]

In Figure 2.8, the results of shear stress controlled viscosity curves are shown. At lower shear stress regions, scattering of viscosities was recorded. These irregularities can be allocated to the chosen measurement setup. At a critical shear stress value, an abrupt change occurred, and

constant viscosity plateaus were reached. Therefore, slippage of the sample can be excluded, since no further shoulders or steps were observed during the transition from high to low viscosities.[23] The plateau values showed the same dependency on m-β-CD concentrations as those obtained in the shear rate controlled measurements shown in Figure 2.7.

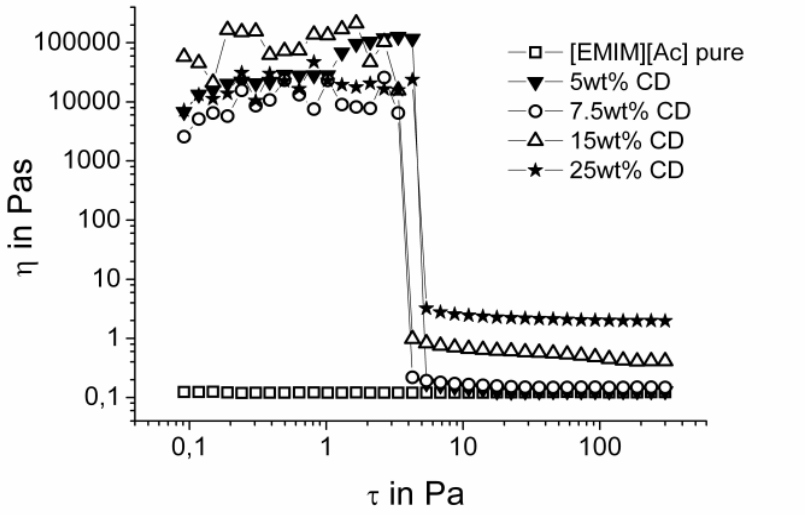


Figure 2.8 Viscosity curves of various m-β-CD/[EMIM][Ac] solutions in comparison to the applied shear stress.

2.2.4 Cox-Merz rule

The empirical rule of Cox and Merz states that the complex oscillation viscosity |η*| and the shear viscosity η agree for polymer melts and homogeneous solutions with no energetic interactions, if they are plotted against angular frequency ω and shear rate Á (Eq. 3), respectively.[24]

$$|\eta^*|(\omega) = \eta(\text{Á}) \tag{3}$$

As Kulicke *et al.* described, derivations from the Cox-Merz rule occur if a superstructure in the relaxed state is destroyed by the imposed shear force.[25] In that case, the complex viscosity |η*| is higher than the shear viscosity η. Figure 2.9 shows a corresponding plot of |η*|, obtained from dynamic oscillatory shear measurements, and η for a 15 wt% solution of m-β-CD in [EMIM][Ac]. This plot confirms strong physical interactions as |η*| is more than a decade

higher than η. Furthermore, the |η*| function rose to an infinitely high value, confirming a gel character and, therefore, form stability at rest.

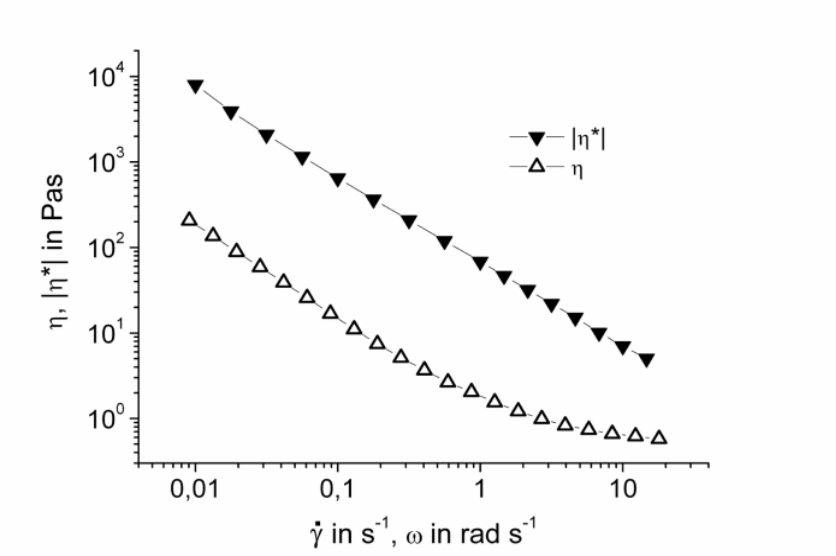


Figure 2.9 Complex oscillation viscosity |η*| and shear viscosity η as a function of the angular frequency ω and the shear rate Á respectively, exemplary for a 15 wt % solution of m-β-CD in [EMIM][Ac] at a shear stress of 0.5 Pa at 23 °C.

2.2.5 Temperature Dependence and Flow Activation Energy

Okoturo and VanderNoot showed that the viscosity of pure ILs is drastically changed by variation of temperature.[26] Therefore, the influence of temperature on the shear-thinning behavior was studied for all weight percentages of m-β-CD. Figure 2.10 shows the temperature dependency of η of a 15 wt% m-β-CD/[EMIM][Ac]-solution. In the region of lower shear rates, the viscosities proceeded independent of the temperature up to 50 °C. Obviously, the physical interactions in the network structure were dominating the hydrodynamic forces in the IL. In contrast to this, a significant decrease of the plateau viscosities could be observed for increasing temperatures. It appears that for higher shear rates, the physical interactions became less important, and the hydrodynamic properties of the IL were prevailing. At temperatures above 50 °C, a decrease in viscosity could already be observed at lower shear rates. This indicates that the gel structure is sensitive to high temperatures and it can be assumed that for temperatures above 70 °C, the curves resemble the Newtonian behavior of pure [EMIM][Ac].

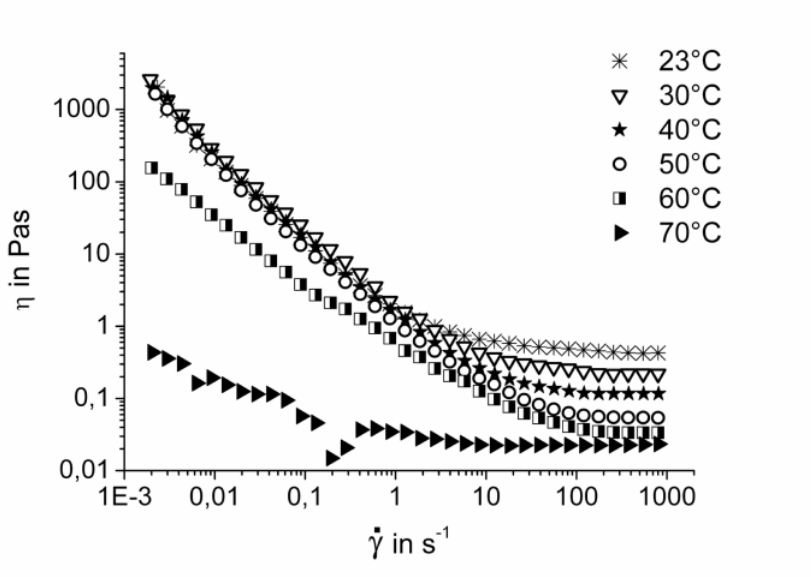


Figure 2.10 Temperature dependence of viscosities for 15 wt% m-β-CD in [EMIM][Ac].

A common way to analyze the viscosity-temperature dependence for non-associating electrolytes is to use the logarithmic form of the Arrhenius equation (Eq. 4),[26] where E_η is the activation energy for viscous flow, R is the universal gas constant and η_∞ is the viscosity at infinite temperature.

$$\ln\eta = \ln\eta_\infty + (E_\eta/RT) \quad (4)$$

Therefore, the values for the plateau viscosities were determined at higher shear rate regions between 23 °C and 50 °C. The results of the Arrhenius plots are shown in Figure 2.11 for all weight percentages of m-β-CD. The flow activation energies could be deduced from the slope of the linear fit of ln(η) versus inverse temperature and are presented in Table 2.2.

The E_η value for pure [EMIM][Ac] was in a good agreement with those already reported in literature for similar ILs (e.g., E_η = 49.33 kJ mol^{-1} for 1-butyl-3-methyl imidazolium acetate [BMIM][Ac] or E_η = 49 kJ mol^{-1} and E_η = 52 kJ mol^{-1} respectively, for [EMIM][Cl]).[27-29]

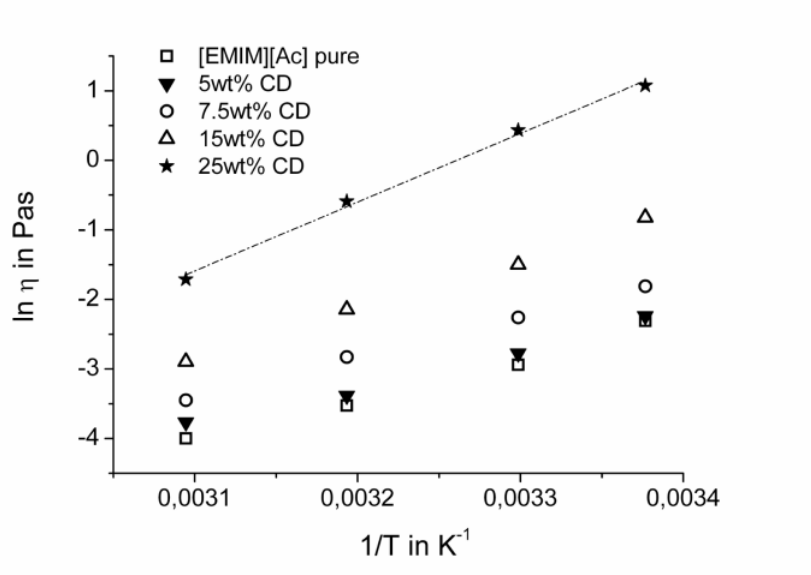


Figure 2.11 Arrhenius plot for m-β-CD/[EMIM][Ac] solutions at different weight percentages. The dashed line corresponds to the Arrhenius approximation.

Table 2.2 Dependency of plateau shear viscosities in mPas and flow activation energies for solutions of m-β-CD in [EMIM][Ac], on weight percentage of m-β-CD and temperature.

wt% m-β-CD	23 °C	30 °C	40 °C	50 °C	E_η [kJ/mol]	R^2
0	99.6	52.9	29.4	18.3	49.19 ± 3.99	0.9806
5	106.5	62.4	34.0	23.2	45.06 ± 3.69	0.9802
7.5	163.6	104.5	59.1	31.8	45.94 ± 1.90	0.9949
15	440.3	223.2	117.3	55.4	59.73 ± 2.62	0.9942
25	2929	1542	554.3	180.7	82.19 ± 3.78	0.9937

As can be seen in Figure 2.12, E_η obtained for low m-β-CD percentages were slightly smaller than E_η of pure [EMIM][Ac] due to the disruption of ionic interactions in the IL. With increasing amounts of m-β-CD a continuous increase of the activation energies could be observed. This behavior can be explained by the increase of the physical interactions between m-β-CD molecules and, therefore, stronger network structures. Since physical interactions of the glucopyranose units of m-β-CD in IL should be the same as for cellulose, the results for E_η were compared to those already reported by Budtova *et al.* [20] for cellulose dissolved in

ILs. It was found that the values of E_η for microcrystalline cellulose (DP = 300) dissolved in [EMIM][Ac] were in the same magnitude as the results shown above and that the flow activation energies also increased with concentration.

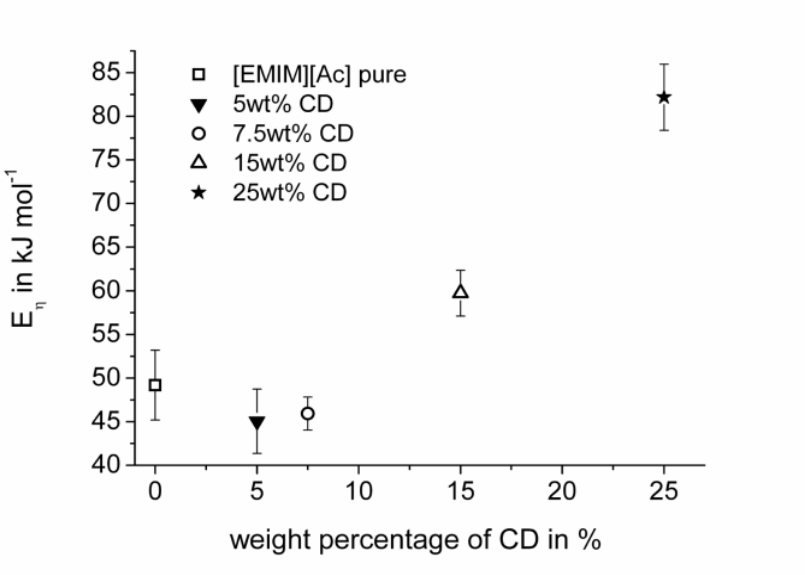


Figure 2.12 Flow activation energy as a function of m-β-CD weight percentage dissolved in [EMIM][Ac].

2.3 Conclusion

The rheological behavior of m-β-CD in [EMIM][Ac] was systematically studied under rotational and oscillatory shear. It was found that even in low m-β-CD concentration, gel structures were formed. Oscillatory measurements showed an abrupt gel-sol transition at certain shear stress values, depending on m-β-CD weight percentages. These processes were both reproducible and reversible. The gel showed a frequency-independent behavior and a structural break-up at very small strains (1 %). In addition, rotational shear experiments revealed the characteristics of gel-like systems with shear-thinning behavior and plateau viscosities, depending on the amount of m-β-CD and the temperature. The comparison of the complex oscillatory viscosity and the shear viscosity according to Cox and Merz verified the existence of a three-dimensional physical network. Furthermore, the temperature dependency of the viscosity was investigated. It was shown that the m-β-CD/[EMIM][Ac] solutions were sensitive to temperatures above 50 °C. Using the logarithmic Arrhenius equation, a correlation

between m-β-CD concentration and flow activation energy could be established. A systematic study involving the network structure of the system is under progress.

2.4 Experimental Details

2.4.1 Materials

1-Ethyl-3-methyl imidazolium acetate [EMIM][Ac] was obtained from BASF SE, Ludwigshafen, Germany. The amount of water and free acid was determined as 4100 ppm by coulometric Karl Fischer titration using Hydranal Coulomat AG from Fluka as anolyte. Randomly methylated (1.8) β-cyclodextrin (m-β-CD, CAVASOL®W7M, technical grade) was obtained from Wacker-Chemie GmbH, Burghausen, Germany. Prior to use, m-β-CD was dried in a CEM Sam 255 microwave drying system and stored in a desiccator under vacuum over sicapent.

2.4.2 Measurements and Methods

Karl Fischer titration was carried out on an 831 KF Coulometer from Metrohm, Deutsche METROHM GmbH & Co. KG, Germany.

[EMIM][Ac] and m-β-CD were mixed in a sealed reaction vessel, and the mixture was stirred at room temperature for at least 24 h under nitrogen atmosphere. Clear solutions were obtained for all applied m-β-CD concentrations varying from 5 to 25 wt%. The complete dissolution was proven by polarization microscope images.

The rheological behavior was studied using a Thermo Scientific HAAKE Mars II rheometer equipped with plate-plate geometry (plate diameter = 35 mm) and a temperature control system DC30/K10 from Thermo scientific to ensure constant temperatures with deviations of ± 0.1 °C. All measurements were carried out with a gap width of 1 mm.

Steady shear measurements were performed for all solutions to achieve flow and viscosity curves. Controlled shear rate tests were performed at varying shear rates from 0.002 to 800 s^{-1} and varying temperatures from 23 °C to 70 °C. Controlled shear stress tests were performed at varying shear stresses from 0.1 to 300 Pa up to a shear rate of 800 s^{-1} and at a temperature of 23 °C.

Oscillatory shear measurements were performed for all solutions to achieve amplitude sweeps and frequency sweeps. Controlled shear stress tests were recorded at a constant frequency (1 Hz) and shear stresses varying from 0.1 to 300 Pa and were additionally performed with cycles of increasing and decreasing shear stress in order to prove reproducibility. Frequency sweeps were recorded at a constant shear stress of 0.5 Pa with frequencies varying from 0.01 to 20 Hz. All oscillatory measurements were performed at 23 °C.

2.5 References

[1] Y. Kawaguchi, T. Nishiyama, M. Okada, M. Kamachi, A. Harada, *Macromolecules* **2000**, *33*, 4472.

[2] H. Ritter, M. Tabatabai, *Prog. Polym. Sci.* **2002**, *27*, 1713.

[3] G. Wenz, B. H. Han, A. Müller, *Chem. Rev.* **2006**, *106*, 782.

[4] J. Szejtli, *Chem. Rev.* **1998**, *98*, 1743.

[5] K. Uekama, F. Hirayama, T. Irie, *Chem. Rev.* **1998**, *98*, 2045.

[6] J. D. Holbrey, K. R. Seddon, *Clean Prod. Processes* **1999**, *1*, 223.

[7] T. Welton, *Chem. Rev*. **1999**, *99*, 2071.

[8] J. S. Wilkes, M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.* **1992**, 965.

[9] K. R. Seddon, *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351.

[10] P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed*. **2000**, *39*, 3773.

[11] P. Bonhôte, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Gratzel, *Inorg. Chem.* **1996**, *35*, 1168.

[12] Q. B. Liu, M. H. A. Janssen, F. van Rantwijk, R. A. Sheldon, *Green Chem*. **2005**, *7*, 39.

[13] S. D. Qi, S. Y. Cui, X. G. Chen, Z. Hu, *J. Chromatogr. A* **2004**, *1059*, 191.

[14] B. Jing, X. Chen, J. C. Hao, H. Y. Qiu, Y. C. Chai, G. D. Zhang, *Colloids Surf. A* **2007**, *292*, 51.

[15] K. Tian, Y. S. Wang, Y. L. Chen, Y. G. Chen, Z. D. Hu, *Talanta* **2007**, *72*, 587.

[16] Y. Zheng, X. Xuan, J. Wang, M. Fan, *J. Phys. Chem. A* **2010**, *114*, 3926.

[17] E. Altin, J. Gradl, W. Peukert, *Chem. Eng. Technol.* **2006**, *29*, 1347.

[18] K. Ueno, S. Imaizumi, K. Hata, M. Watanabe, *Langmuir* **2009**, *25*, 825.

[19] H. B. Kim, J. S. Choi, S. T. Lim, H. J. Choi, H. S. Kim, *Synth. Met.* **2005**, *154*, 189.

[20] M. Gericke, K. Schlufter, T. Liebert, T. Heinze, T. Budtova, *Biomacromolecules* **2009**, *10*, 1188.

[21] N. Agmon, *J. Phys. Chem.* **1996**, *100*, 1072.

[22] G Wenz, *Angew. Chem*. **1994**, *106*, 851.

[23] G. P. Roberts, H. A. Barnes, *Rheol. Acta* **2001**, *40*, 499.

[24] W. P. Cox, E. H. Merz, *J. Polym. Sci.* **1958**, *28*, 619.

[25] C. Clasen, W. M. Kulicke, *Prog. Polym. Sci.* **2001**, *26*, 1839.

[26] O. O. Okoturo, T. J. VanderNoot, *J. Electroanal. Chem.* **2004**, *568*, 167.

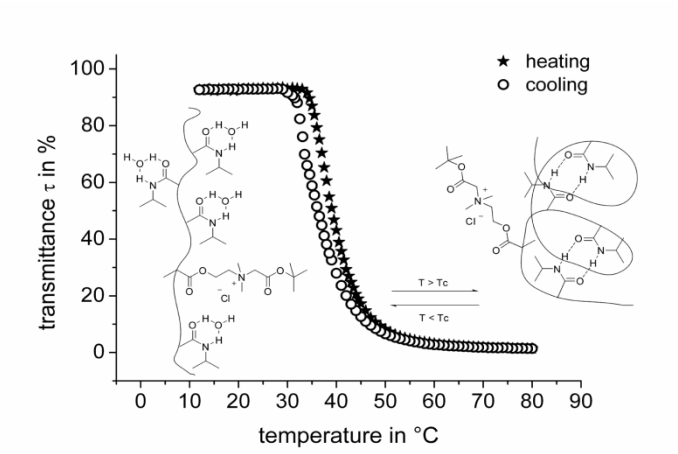
[27] C. Rey-Castro, L. F. Vega, *J. Phys. Chem. B* **2006**, *110*, 14426.

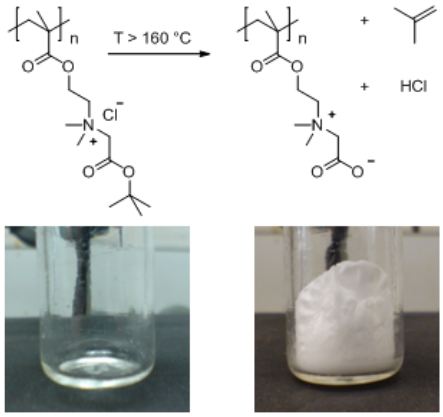
[28] K. G. Bogolitsyn, T. E. Skrebets, T. A. Makhova, *Russ. J. Gen Chem.* **2009**, *79*, 125.

[29] K. R. Seddon, A. Stark, M. J. Torres, *Clean Solvents* **2002**, *819*, 34.

Chapter 3

Ionic Liquid-Derived Thermal-Sensitive and Foamable Polyelectrolytes





Abstract

The synthesis of the easily decomposable ionic monomer 2-*tert*-butoxy-*N*-[2-(methacryloyl-oxy)ethyl]-*N*,*N*-dimethyl-2-oxoethanammonium chloride (**3**) via thermally induced syn-elimination of a *tert*-butyl ester group, was realized simply by mixing *N*,*N*-dimethyl-aminoethyl methacrylate (**1**) and *tert*-butyl chloroacetate (**2**) at ambient temperature without solvent. The obtained salt was polymerized via free radical polymerization. The decomposition and foaming via *iso*-butene formation takes place by heating up to about 160 °C. IR, DSC, TGA and GC/MS measurements were accomplished to follow this pyrolysis reaction. Furthermore, the copolymerization of **3** with *N*-isopropylacrylamide (NiPAAm, **5**) was carried out with different monomer ratios. Molar mass distributions were measured using an asymmetrical flow field-flow fractionation (aF^4) system. The obtained copolymers **6-10** exhibit a lower critical solution temperature (LCST) behavior in water with cloud points at different temperatures depending on the monomer ratio.

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3 Ionic Liquid-Derived Thermal-Sensitive and Foamable Polyelectrolytes

3.1 Introduction

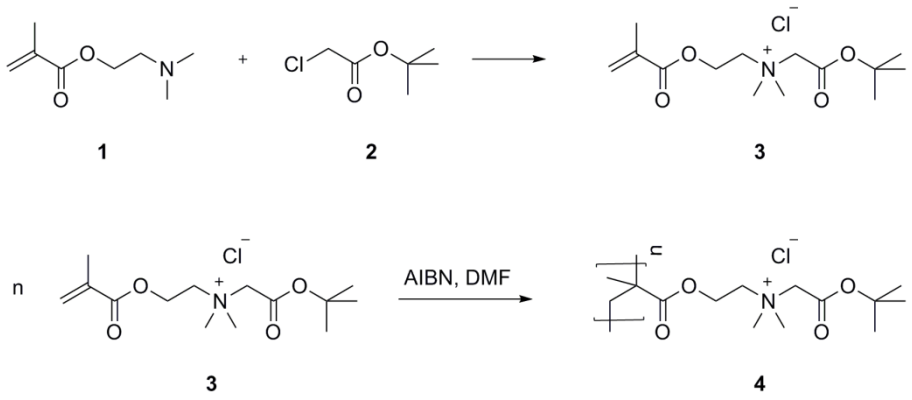
Currently, foamed polymeric materials are used for various applications such as transportation packing, thermal insulation, as well as weight reducing constructive elements in the automotive and aviation sector. Generally, a common foamable polymer consists of a basic polymer, an expending agent such as carbon dioxide, low boiling hydrocarbons or nitrogen gas and additives.[1] The foaming by means of an instant intramolecular ester pyrolysis in the polymer is an interesting alternative.[2] High temperatures up to 300 °C are necessary which may lead to decomposition of the polymer. However, the insertion of electronegative substituents, such as ammonium groups should facilitate this elimination reaction by lowering the required temperature.[3,4] Therefore, the development of new polyelectrolytes containing thermally sensible *tert*-butyl ester groups offers a new pathway to design self-foamable materials.

Poly(*N*-isopropylacrylamide), belongs to a highly investigated class of polymers which become insoluble in water above a critical temperature (T_c).[5] This lower critical solution (LCST) behavior can be controlled by changing the pH value,[6] electric field, ionic strength,[7] by copolymerization,[8,9] chemical modification, or especially due to supramolecular interactions with cyclodextrins.[10-12] In the following, the synthesis of a new thermally decomposable ionic methacrylic monomer and the copolymerisation with NiPAAm for model studies is presented.

3.2 Results and Discussion

The nucleophilic aliphatic substitution reaction between *tert*-butyl-chloroacetate (**2**) and *N*, *N*-dimethyl-aminoethyl methacrylate (**1**) is shown in Scheme 3.1. The reaction led to the formation of the desired salt 2-*tert*-butoxy-*N*-[2-(methacryloyl-oxy)ethyl]-*N*,*N*-dimethyl-2-oxoethan ammonium chloride (**3**) in a nearly quantitative yield.

After purification, the monomer was polymerized via free-radical mechanism in DMF as solvent using AIBN as initiator. The average molar mass (M_n) of the obtained hydrophilic polymer **4** was around 36 kDa according to asymmetrical flow field-flow fractionation (aF^4) measurements.



Scheme 3.1 Synthesis and polymerization of monomer **3**.

It was expected that high temperature treatment of bulky polymer **4** should lead to a formation of gaseous isobutylene in the polymer matrix. Analogously, we recently showed that electron withdrawing imidazolium groups activates such ester groups also in respect to microwave heating.[3] Accordingly, the syn-elimination during classical thermal heating took place at relatively reduced temperature around 160 °C yielding a polymeric foam **4a** (Figure 3.1).

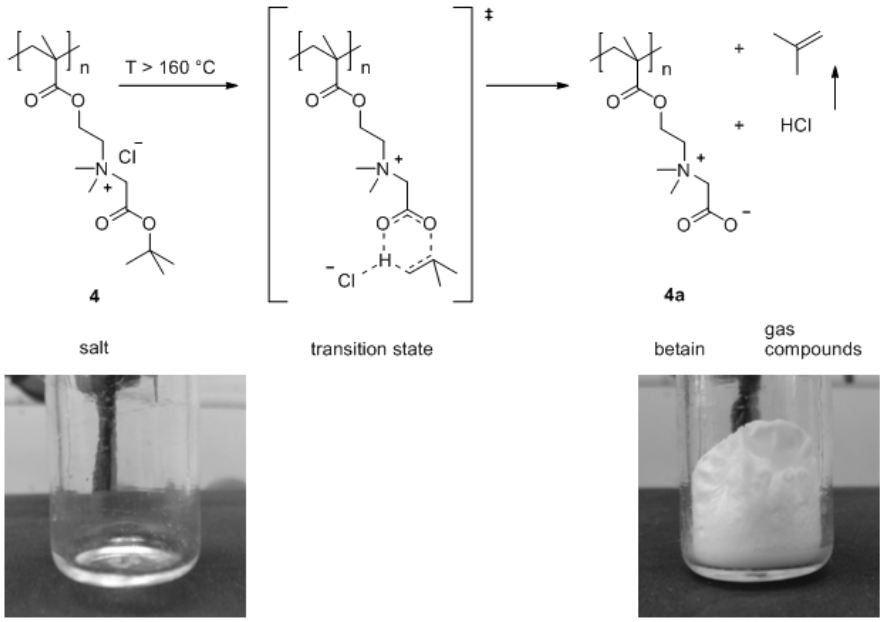


Figure 3.1 Foaming of polymer **4** to polymeric foam **4a** by thermal induced ester pyrolysis.

FT-IR measurements of **4** showed a characteristic broad band for the stretching mode of both ester C=O bonds at around 1732 cm^{-1}, shifting to a lower frequency at 1722 cm^{-1} of the polymethacrylic ester after the foaming took place. Furthermore, a band for the new formed carboxylate anion at 1635 cm^{-1} and a band for the C-H bending mode of enclosed isobutylene gas at 889 cm^{-1} appeared in the recorded spectrum of **4a**.

To evaluate the temperature profile of the ester pyrolysis of the polymeric salt **4,** DSC experiments were carried out over the temperature range from 25 up to 250 °C. It turned out that at 150 °C a sharp endothermic peak appeared, followed by a second broad endothermic peak at 220 °C. Both peaks indicate the occurrence of successive ester pyrolysis and further decomposition reactions, respectively. A simple melting process can be excluded due to the amorphous character of the polymeric material. In addition, no peaks appeared during a cooling and second heating run. To further prove the formation of isobutylene as a result of the ester pyrolysis, GC/MS studies of **4** were carried out. Therefore, the solid and dry polymer **4** was placed in a glass vial, sealed and heated up to 160 °C. The obtained gas was taken out by a syringe and characterized. The signal at a retention time of 0.45 min in the gas chromatogram can be definitely identified as isobutylene with a molecular weight of 56 g mol^{-1}. Apparently, temperatures above 180 °C led to the formation of chlorinated by-products in the gas phase. The thermogravimetric analysis (TGA) of homopolymer **4** is shown in Figure 3.2.

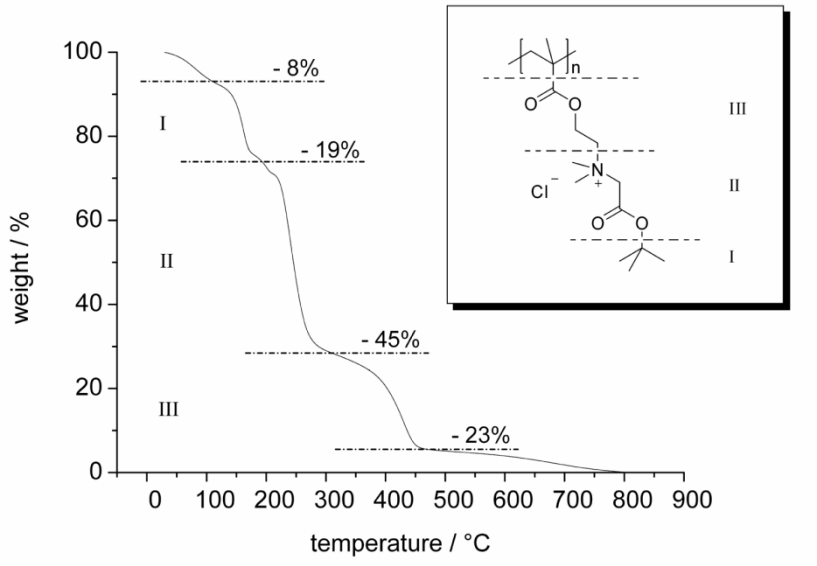
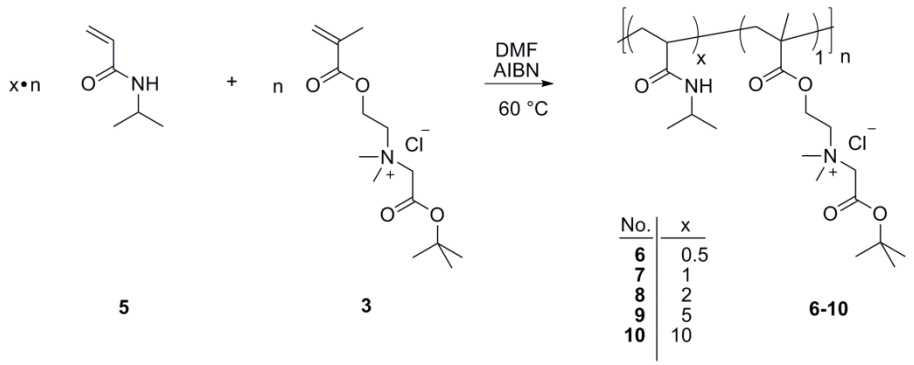


Figure 3.2 Thermogravimetric analysis of homopolymer **4**.

The weight loss of less than 10 % at temperatures below 100 °C was due to the extrusion of water. A considerable decomposition of the material began at temperatures above approximately 120 °C. The weight loss of 19 % exactly corresponded to the pyrolysis of the *tert*-butyl group. It can be assumed that at above 200 °C, the partial structure of the ammonium group was cleaved (weight loss: 45 %), followed by the cleavage of the ester group linked to the backbone (weight loss: 23 %) at above 335 °C. Temperatures above 500 °C led to the destruction of the polymer backbone

In addition to the homopolymerization, Monomer **3** was also copolymerized with NiPAAm (**5**) at different molar ratio in DMF using AIBN as radical initiator yielding the copolymers **6-10** (Scheme 3.2). The copolymer composition of **6-10** were determined by ^{1}H-NMR spectroscopy where the integrals of the signals at 3.29 ppm (6H, -N^{+}(C**H$_3$**)$_2$-) and 1.05 ppm (6H, NHCH(C**H$_3$**)$_2$) were compared. As expected, due to the high conversion of the monomers the obtained ratios of incorporated units in the copolymers were very similar to the applied monomer ratios. Beyond that, **6-10** were characterized by FT-IR spectroscopy, DLS and turbidity measurements. Some characteristics of these polymers (**4** and **6-10**) are listed in Table 3.1. All polymers **4, 6-10** were soluble in water at room temperature. Turbidity measurements of the copolymers **6-10** showed clearly that the aqueous polymer solutions exhibit a reversible LCST-behaviour at elevated temperatures. A relatively high fraction of salt is necessary to shift the clouding point to significantly higher temperatures (Table 3.2).



Scheme 3.2 Free radical copolymerization of monomer **3** with NiPAAm **5** at different molar ratios.

Table 3.1 Experimental data for homopolymer **4** and copolymers **6-10**.

Polymer	X[a)]	M_n[b)] [g·mol^{-1}]	M_w/M_n
4	0	36 200	1.9
6	0.5	43 700	1.3
7	1	48 400	1.2
8	2	34 100	1.7
9	5	37 100	1.3
10	10	32 300	1.9

a) x = n(5) / n(3); b) determined by aFFFF-measurements

Table 3.2 Cloud point temperature in dependence of the molar ratio of NiPAAm in the co-polymers.

Polymer	X[a)]	cloud-point [°C]
6	0.5	- [b)]
7	1	55
8	2	39
9	5	36
10	10	34

a) x = n(5) / n(3); b) no cloud point observed between 10 to 80 °C

As expected, for homopolymer **4** and copolymer **6** (x = 0.5) no LCST behavior was observed. However, an increasing molar amount of NiPAAm led to a decreasing hydrophilic character of the copolymers and, thus, reduced the solubility in water. Accordingly, Figure 3.3 shows the shift of the cloud point of the copolymers depending on the molar ratio from 34 °C up to 55 °C. LCST measurements corresponding to the molecular weight dependence were not focus of this work.

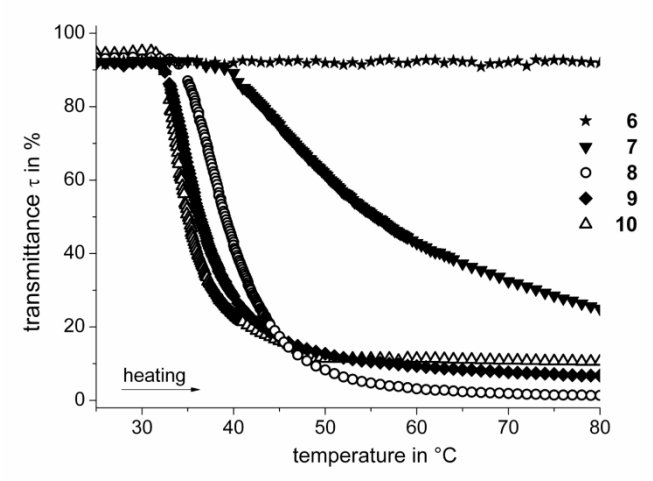


Figure 3.3 Transmittance τ of the aqueous solutions of **6-10** at pH = 7, compared to temperature in a range between 10 and 80 °C (heating rate 1°C min^{-1}).

Since the solubility of the polymers is reflected in the LCST values, also the hydrodynamic diameters of the copolymers dissolved in aqueous solutions should be dependant on the temperature. As an example, Figure 3.4 shows the transmittance and the hydrodynamic diameter as a function of the temperature in a range of 25 to 45 °C for a 0.5 wt% aqueous solution of **10**. At temperature above T_c, polymer aggregation took place. The polymer precipitated and as a result the hydrodynamic diameter increased up to 300 nm.

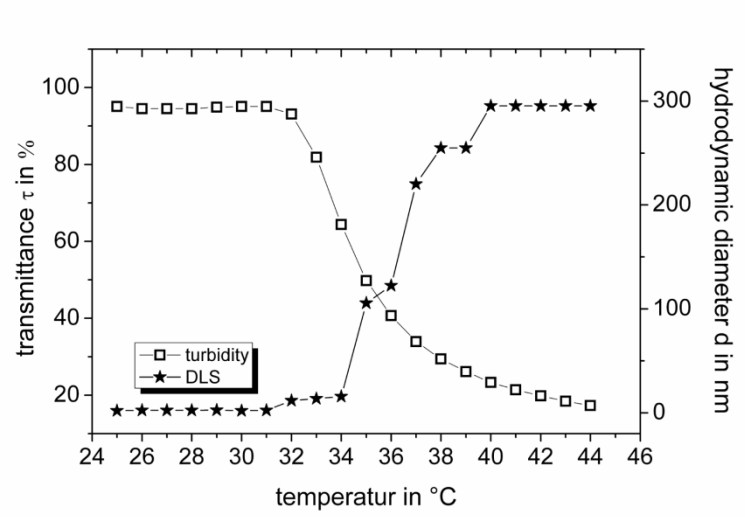


Figure 3.4 Transmittance τ and hydrodynamic diameter d as a function of temperature for an aqueous 0.5 wt% solution of copolymer **10**.

3.3 Conclusion

The synthesis of the foamable polyelectrolyte **4** was described. Therefore, monomer **3** was synthesized simply by mixing *N*,*N*-dimethylaminoethyl methacrylate (**1**) and *tert*-butyl chloroacetate (**2**) at ambient temperature without solvent and polymerized free radically with AIBN in DMF. Heating treatment of the polymer compound led to a cleavage of isobutylene which foams the material. GC/MS, DSC, IR and TGA measurements have prove the postulated formation of gaseous isobutylene. Furthermore, the copolymerization of **3** with NiPAAm (**5**) was investigated to obtain copolymers with T_c values between 34 °C and 55 °C.

3.4 Experimental Details

3.4.1 Materials

All reagents and reactants used were commercially available and used without further purification.

3.4.2 Measurements and Methods

The structures of the synthesized monomer and polymers were proven by ^{1}H- and ^{13}C-NMR spectroscopy using a Bruker Avance DRX 500 spectrometer at 500.13 MHz for proton and 125.77 MHz for carbon. Using DMSO-d_6 as solvent, chemical shifts were referenced to the solvent value at δ_H = 2.51 ppm and δ_C = 39.52 ppm, respectively. Copolymer constitutions were determined by using ^{1}H-NMR spectroscopy.

C, H, N - elemental analysis was determined using a Perkin Elmer 2400 CHN analyzer.

Infrared spectra were recorded on a Nicolet 5SXB FT-IR spectrometer, equipped with an ATR unit.

Gas chromatography/mass spectrometry (GC/MS) measurements were accomplished on a Thermo Finnigan Trace DSQ system. The ionization occurred by means of electron impact (EI).

Pyrolysis temperatures (T_p) were measured by a Mettler Toledo DSC 822e equipped with a sample robot TSO801RO. The apparatus was controlled over a temperature range between

298.15 and 523.15 K at a heating rate of 10 K min^{-1}. For calibration, standard tin, indium, and zinc samples were used.

Molar mass distributions measurements were carried out at 25 °C using the commercial asymmetrical flow field-flow fractionation System Eclipse 2 (Wyatt Technology Europe, WTE, Dernbach, Germany). The eluent flow was provided by a solvent reservoir, an on-line degasser, isocratic pump, and auto injector (Agilent 1200 series). A short channel equipped with polyethersulfonate membrane (MWCO 10 kDa, WTE) and a 250 µm spacer (WTE, type wide) was used. 30 µl of the sample solution (c = 1 mg ml^{-1}) was injected into the channel. The separations were carried out using an elution profile with a flow rate V=1.0 ml min^{-1} and an ambient cross-flow. The outlet of eclipse 2 was connected to the miniDAWN treos three-angle light scattering photometer followed by an Optilab rEX dRI detector.

Thermogravimetric analyses (TGA) were carried out with a TA 600 Perkin Elmer (TGA combined with a DTA) over a temperature range between 303.15 and 1073.15 K under argon atmosphere. The heating rate was 10 K min-1. All measurements were baseline corrected and were analyzed by Pyris software.

Turbidity measurements were determined using a TP1 turbidity photometer over a temperature range of 10 to 80 °C. 0.015 g of each polymer was dissolved in 2985 µl of water. During continuous stirring, the transparency of the sample was determined by a voltage controlled semiconductor laser and a silicon photodiode at a wavelength of 500 nm and a heating or cooling rate of 1 °C min^{-1}. All critical temperatures were detected by determination of the temperature where the transparency of the solution was decreased to 50 % of the initial value.

Dynamic Light Scattering (DLS) experiments were carried out with a Malvern Nano ZS ZEN 3600 in a temperature range from 25 to 45 °C. The particle size distribution was derived from a deconvolution of the measured intensity autocorrelation function of the sample by the NNLS general purpose mode algorithm included in the DTS software.

For the foaming experiments, **4** was dissolved in methanol and was transferred into a flat grounded vial. The solvent was evaporated at 60 °C overnight to obtain a transparent film. It was heated to 160 °C to obtain the foamed polymer **4a**.

3.4.3 Synthesis of 2-*tert*-butoxy-*N*-[2-methacryloyloxyethyl]-*N*,*N*-dimethyl-2-oxo ethan ammonium chloride, 3

Monomer **3** was synthesized by mixing *N*, *N*-dimethylaminoethyl methacrylate (**1**) (5g, 0.032 mol) and *tert*-butyl chloroacetate (**2**) (5.73g, 0.038 mol). The mixture was stirred at room temperature under nitrogen atmosphere overnight. The raw product was diluted, filtered, and washed with acetone several times before it was washed with diethyl ether. The purified product was dried under vacuum to obtain a white solid.

Yield 9.55 g (97 %)

mp. 156 °C (pyrolysis)

IR (cm^{-1}) 3006, 2978, 2943 (CH_2, CH_3); 1742, 1716 (C=O, ester groups); 1641 (C=C); 1457 (CH_2, CH_3 bending); 1394, 1369 (-$C(CH_3)_3$); 1151 (CO)

^{1}H NMR δ/ppm (500 MHz, DMSO-d_6) = 6.11 (s, 1H, $\mathbf{H_2}C=C(CH_3)$-); 5.80 (s, 1H, $\mathbf{H_2}C=C(CH_3)$-); 4.58 (m, 4H, -$C\mathbf{H_2}$-CH_2-$N^+(CH_3)_2$-$C\mathbf{H_2}$-); 4.00 (m, 2H, -CH_2-$C\mathbf{H_2}$-$N^+(CH_3)$-); 3.34 (s, 6H, -$N^+(C\mathbf{H_3})_2$-); 1.94 (s, 3H, $H_2C=C(C\mathbf{H_3})$-); 1.50 (s, 9H, -O-$C(C\mathbf{H_3})_3$)

^{13}C NMR δ/ppm (125 MHz, DMSO-d_6) = 166.79 (-CH_2-**C**OO-); 164.92 (CH_2=$C(CH_3)$-**C**OO-); 136.25 (CH_2=**C**(CH_3)-); 127.57 (**C**H_2=(CH_3)-); 85.07 (-O-**C**$(CH_3)_3$); 63.47 (-CH_2-**C**H_2-$N^+(CH_3)_2$-); 62.59 (-$N^+(CH_3)_2$-**C**H_2-COO-); 59.18 (-O-**C**H_2-CH_2-); 52.48 (-N^+(**C**$H_3)_2$-); 28.53 (-O-$C($**C**$H_3)_3$); 18.83 (CH_2=$C($**C**$H_3)$-)

C, H, N $C_{14}H_{26}NO_4Cl$ (307.81):

calc. (%):	C: 54.63	H: 8.52	N: 4.55
found (%):	C: 54.80	H: 8.43	N: 4.47

3.4.4 Syntheses of the polymers

Synthesis of homopolymer 4

2 g (6.5 mmol) of **3** were dissolved in DMF (8.4 ml). After purging the solution with nitrogen for 20 min AIBN (10.7 mg, 1 mol-% = 0.065 mmol) was added as a radical initiator. The solution was stirred at 60 °C (oil bath) overnight. The polymer was precipitated in diethyl ether, filtered off and dried under vacuum. The dry polymeric material was redissolved in water, dialyzed, and freeze dried.

IR (cm^{-1}) 2974, 2933, 2876 (CH_2, CH_3); 1732 (C=O, ester groups); 1475 (CH_2, CH_3 bending); 1369, 1396 (-$C(CH_3)_3$); 1151 (CO)

^{1}H NMR δ/ppm (500 MHz, DMSO-d_6) = 4.31 (s (br), 4H, -O-CH_2-**CH_2**-$N^+(CH_3)_2$-**CH_2**); 3.98 (s (br), 2H, -O-**CH_2**-CH_2-$N^+(CH_3)_2$-CH_2); 3.34 (s (br), 6H, -N^+(**CH_3**)$_2$-); 1.90 (s (br), 2H, backbone-CH_2); 2.28-1.75 (s (br), 9H, -O-C(**CH_3**)$_3$); 1.31-0.75(s (br), 3H, backbone-CH_3)

M_n 36 kDa

Synthesis of copolymers 6-10

N-isopropylacrylamide (NiPAAm, **5**) (2.5 g, 0.022 mol) was dissolved in DMF (20 ml). The particular salt **3**, was added in molar ratios of n(salt) : n(NiPAAm) of 1:10 (n(salt) = 0.0022 mol), 1:5, 1:2, 1:1 and 2:1. After purging the solution with nitrogen for 20 min, AIBN (40 mg, 1 mol% = 0.24 mmol) was added as a radical initiator. The solution was stirred at 60 °C (oil bath) overnight. The polymer was precipitated in diethyl ether, filtered off and dried under vacuum. The obtained copolymers were redissolved in water, dialyzed and freeze dried.

IR (cm^{-1}) 3433, 3282, 3068 (-CONH-); 2971, 2933, 2875 (CH_2, CH_3); 1733 (C=O, ester groups); 1638 (amid I); 1536 (amid II); 1457 (CH_2, CH_3 bending); 1129 (CO)

^{1}H NMR δ/ppm (500 MHz, DMSO-d_6) = 4.51-3.88 ((br), 6H, -C**H$_2$**C**H$_2$**-$N^+(CH_3)_2$-C**H$_2$**); 3.79 (s (br), 1H, -NH-C**H**$(CH_3)_2$); 3.29 (s (br), 6H, -$N^+(CH_3)_2$-); 2.28-1.73 ((br), backbone -CH_3, -CH_2-); 1.44 (s (br), 9H, -O-C(C**H$_3$**)$_3$); 1.05 (s (br), 6H, -NH-CH(C**H$_3$**)$_2$)

M_n for **6**, **7**, **8**, **9,** and **10** were 43, 48, 34, 37, and 32 kDa, respectively.

3.5 References

[1] US 5482977 (**1996**), invs.: R. L. McConnell, K. C. Khemani.

[2] H. Ritter, S. Schwarz-Barac, P. Stein, *Macromolecules* **2003**, *36*, 318.

[3] S. Amajjahe, H. Ritter, *Macromol. Rapid Commun.* **2009**, *30*, 94.

[4] G. G. Smith, D. A. K. Jones, *J. Org. Chem.* **1963**, *28*, 403.

[5] H. Feil, Y. H. Bae, J. Feijen, S.W. Kim, *Macromolecules* **1993**, *26*, 2496.

[6] J. Zhang, N. A. Peppas, *Macromolecules* **2000**, *33*, 102.

[7] H.-C. Chin, Y.-F. Lin, S.-H. Hung, *Macromolecules* **2002**, *35*, 5235.

[8] L. D. Taylor, L. D. Cerankowski, *J. Polym. Sci. Polym. Chem. Ed.* **1975**, *13*, 2551.

[9] T. Trellenkamp, H. Ritter, *Macromol. Rapid Commun.* **2009**, *30*, 1736.

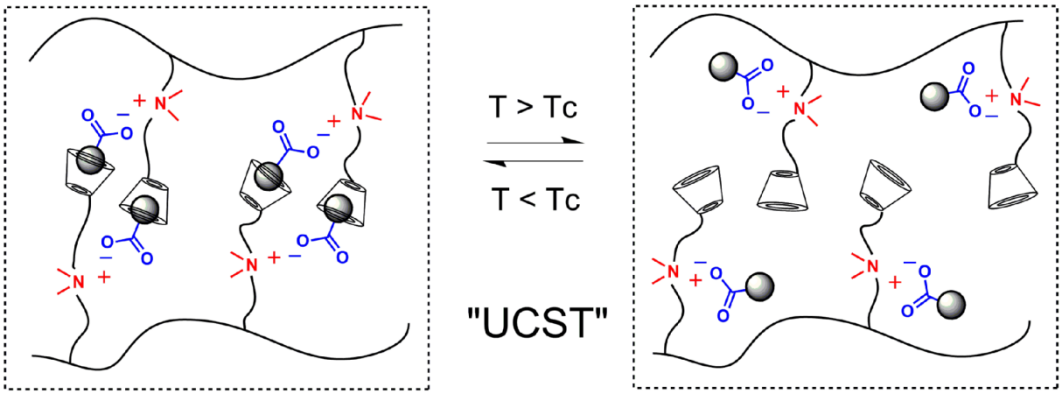
[10] S. Schmitz, H. Ritter, *Angew. Chem. Int. Ed*. **2005**, *44*, 5658.

[11] O. Kretschmann, C. Steffens, H. Ritter, *Angew. Chem. Int. Ed.* **2007**, *46*, 1.

[12] O. Kretschmann, S. W. Choi, M. Miyauchi, I. Tomatsu, A. Harada, H. Ritter, *Angew. Chem. Int. Ed.* **2006**, *45*, 4361.

Chapter 4

Novel Cyclodextrin Containing Poly(Pseudo-Betaines)



Abstract

A novel monofunctional β-cyclodextrin monomer was synthesized via copper(I)-catalyzed azide/alkyne click reaction and further polymerized by free radical polymerization. The obtained cyclodextrin containing polyelectrolyte can be used as a novel intriguing polymeric host for smart supramolecular assembling systems. By inclusion complexation of adamantyl carboxylate as a model guest, pseudo-betaine structures with UCST-behavior were obtained. Furthermore, the complex stability constants were determined by isothermal titration calorimetry at different temperatures.

Parts of this chapter will be published: N. Gonsior, H. Ritter, submitted.

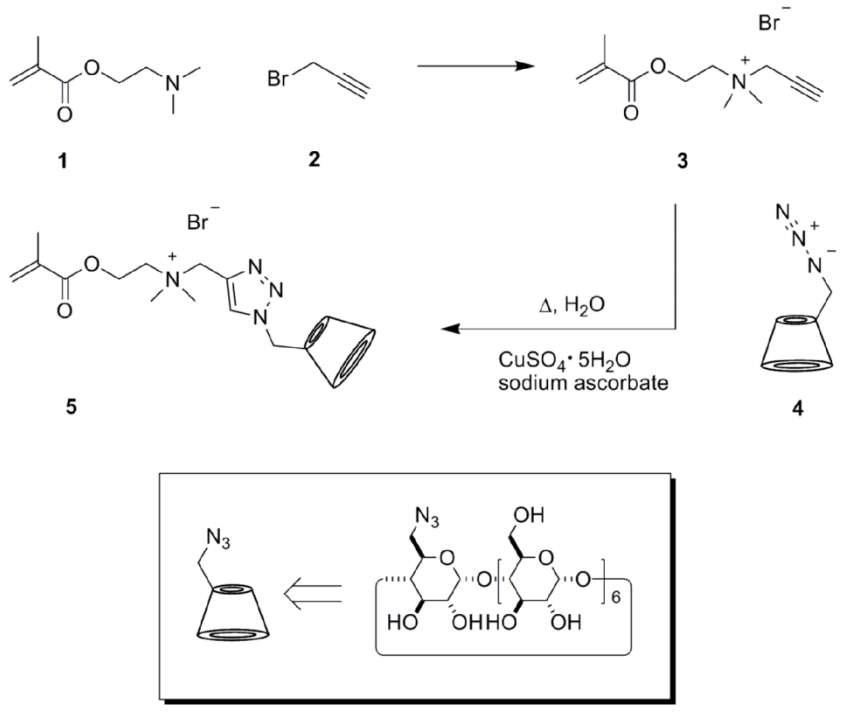
4 Novel Cyclodextrin Containing Poly(Pseudo-Betaines)

4.1 Introduction

The copper(I)-catalyzed azide/alkyne click reaction (CuAAc) introduced by Sharpless and Meldal independently in 2002,[1,2] represents a variation of Huisgens 1,3 dipolar cycloaddition reaction. Major benefits of CuAAc reactions are the acceleration of reaction rate, higher yields, and the modularity and wideness in scope. The aromatic triazole is formed exclusively as the 1,4-isomer and is stable against oxidation, reduction, and hydrolysis.[3] Furthermore, these reactions can be carried out under mild conditions (20-70 °C) in bulk, protic, or aprotic solvents. Since the early reports in polymer science, published in 2004,[4-8] the concept of click chemistry has had enormous impact within the field of polymer science. But until now, there is only a small number of monofunctional β-cyclodextrin monomers, which have been prepared by use of CuAAc.[9,10] Hydrophilic polymers with a so-called lower critical solution temperature (LCST) are often described in literature.[11-19] But there are only a few reports concerning polymers which have an upper critical solution temperature (UCST) in aqueous solutions. [20-22] Yui *et al.* reported, that inclusion complexes of β-cyclodextrin conjugated poly(ε-lysine) with 3-trimethylsilylpropionic acid form supramolecular assemblies, which showed a rapid response on the UCST behavior by a small change of pH or temperature.[23] Furthermore, reversible self-association was observed in certain polyzwitterionic hydrogels that display an USCT. At high temperature the dipolar interactions broke to yield isolated polymer chains that were completely solvated.[24] The first synthesis of a zwitterionic polymer was described in 1957.[25] Polyzwitterions and polybetaines, respectively, belong to a special class of polyampholytes, where each monomer carries both the positive and negative charges.[25-29] An extended inquiry through literature reveals, that only covalent betaine structures are described. Until now, there has been no investigation on the formation of betaine structures via supramolecular host/guest interactions. In this study, thus, the synthesis and characterization of a novel β-cyclodextrin containing polyelectrolyte is described. Furthermore, the properties and the ability to form betaine structures due to supramolecular host/guest interactions are investigated.

4.2 Results and Discussion

A new β-cyclodextrin (β-CD) containing polyelectrolyte **6,** forming inclusion complexes with various guest molecules, was obtained via free radical polymerization of monomer **5**, which was prepared according to Scheme 4.1. The intermediate *N*,*N*-dimethyl-[2-(2-methyl-acryloyloxy)-ethyl]-prop-2-ynyl-ammonium bromide (**3**) was obtained from nucleophilic substitution reaction between *N*,*N*-dimethylaminoethyl methacrylate (**1**) and propagyl bromide (**2**). The Cu-mediated "click reaction" of **3** with mono-6-azido-6-deoxy-β-cyclodextrin (**4**) in water led to formation of the ionic β-CD containing monomer **5**. The active copper(I) catalytic species was generated in situ by reduction of $CuSO_4$ with sodium ascorbate. Under the applied conditions, the yield of **5** was about 90 %. Cu-impurities could be easily removed by the addition of pentaerythrit-tetrakis-(3-mercapto-propionat). The obtained Cu-complex precipitates in water and could be separated by filtration.



Scheme 4.1 Synthesis of monofunctional β-CD monomer **5**.

The cycloaddition reaction was confirmed by IR and NMR spectroscopy as well as MALDI-TOF mass spectrometry. The specific IR bands for azide and triple bond at 2103 and 2123 cm^{-1} respectively disappeared. Furthermore, the formation of the triazole ring was proven by ^{1}H-NMR spectroscopy (Figure 4.1). Only 1,4-disubtituted 1,2,3-triazoles were formed selec-

tively with high yield.[1] The 4-*H*-1,2,3-triazole proton was distinguished at 8.37 ppm. The molecular weight was investigated by MALDI-TOF mass spectrometry. A single mass peak at m/z ratio = 1355.6 was detected for monomer **5** cation without bromide counter ion.

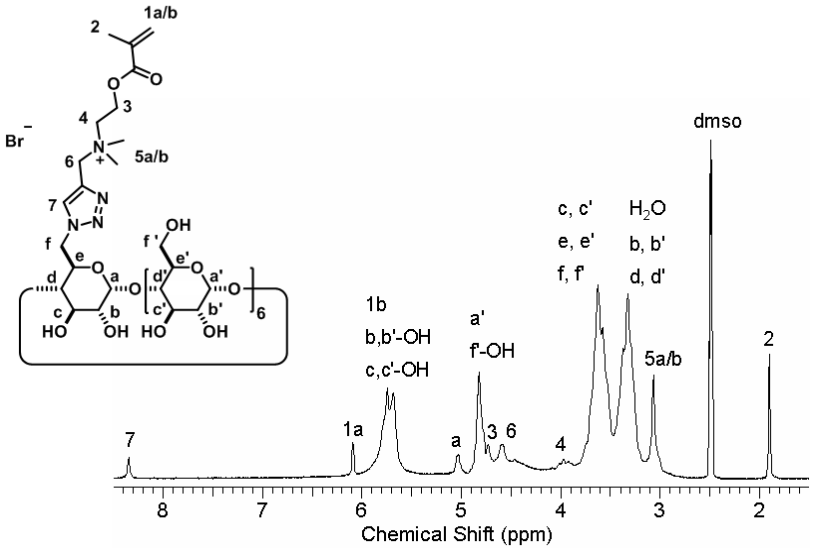
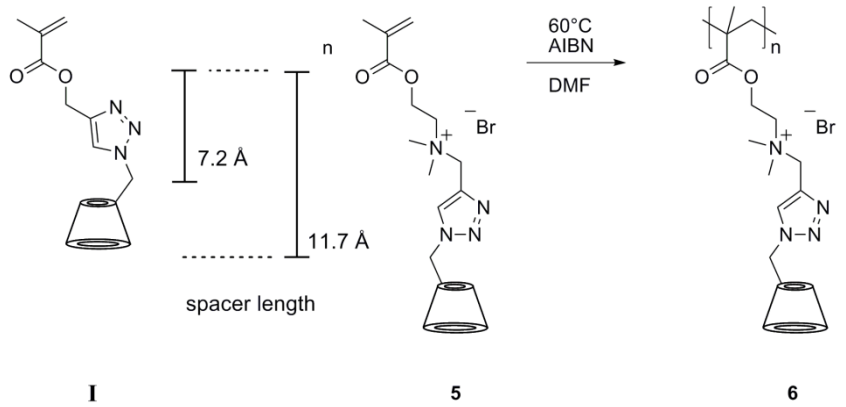


Figure 4.1 ^{1}H-NMR spectrum of **5** (500 MHz, DMSO-d_6).

Earlier attempts to polymerize a similar non-ionic monofunctional cyclodextrin methacrylate (**I**) resulted in the formation of water soluble oligomers.[9] Only by copolymerization with N-isopropyl-acrylamide new copolymers with a lower critical solution temperature (LCST) behavior and the ability to enclose guest molecules could be obtained.[30,31] Furthermore, a research through literature reveals that the average molecular weight (M_n) of homopolymers obtained via radical polymerization of different monofunctional CD-monomers do not exceed 13 000 g mol^{-1} which is consistent with a low average degree of polymerization (DP) of < 12.[32-34] In contrast, the free radical polymerization of monomer **5** led to a M_n of polymeric salt **6** of around 59 000 g mol^{-1} (PD ≈ 40). With a value of 1.4, the polydispersity was unusually low for a radical polymerization. It can be assumed that the dialysis step after polymerization led to a narrow molecular weight distribution and was not further investigated. This enhancement of polymerization properties is supposed to be a result of spacer length as indicated in Scheme 4.2.



I **5** **6**

Scheme 4.2 Free-radical polymerization of **5** yielding water soluble polyelectrolyte **6** and comparison of the spacer length between **5** and monofunctional CD methacrylate **I**. [9, 30,31]

The molecular weight distribution of **6** was determined by asymmetric flow field flow fractionation (aFFFF) separation technique, combined with a three angle static light scattering (MALS) detector to achieve absolute molecular weights. Figure 4.2 depicts the aFFFF-MALS elution diagram for **6** and further the determination of the refractive index increment. The detected UV-signal was in excellent agreement with the signal for the refractive index, indicating that each repeating unit was bearing a triazole and cyclodextrin moiety respectively.

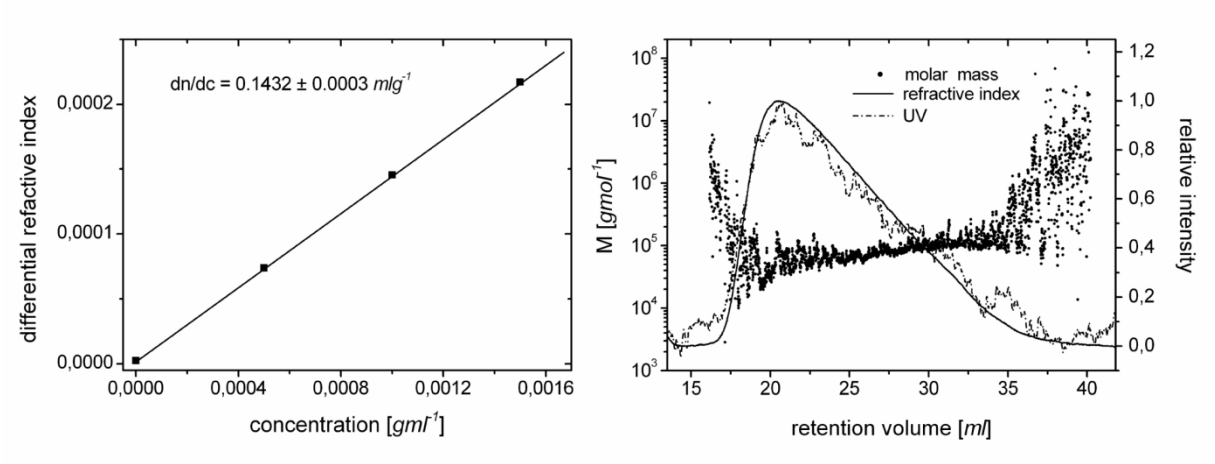
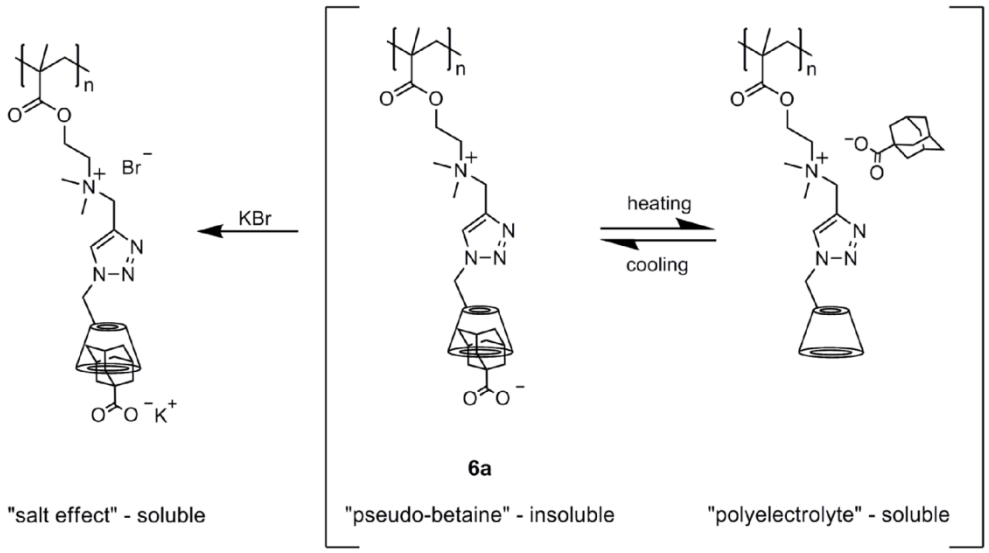


Figure 4.2 (left) Determination of the refractive index increment (dn/dc) for **6** in 0.1 M aqueous KBr solution. (right) Elution diagram for **6** as it is followed by refractive index and UV-detector at $\lambda = 256$ nm, respectively. Furthermore, the molecular weight is plotted versus elution time.

According to our interest in supramolecular chemistry, the ability of polymer **6** to form inclusion complexes was investigated. Therefore, potassium adamantyl carboxylate (AdCOOK) was added in an equimolar amount to an optically clear aqueous solution of polymer **6**. Surprisingly, a sudden turbidity after that addition was observed. However, after heating the dispersion above 60 °C, transparency was completely recovered. In contrast, a 0.1 M potassium bromide (KBr) solution of the polymer/AdCOOK complex **6a** was completely soluble in a temperature range from 10 up to 80 °C (Scheme 4.3).



Scheme 4.3 Solubility properties of complexed polymer **6a** depending on temperature and salt content in aqueous solutions.

It is well established that β-CDs and adamantyl-groups form stable 1:1 complexes in water at ambient temperature.[35] Furthermore, it is known that polybetaines are insoluble in water but also that the addition of salt can enhance the solubility of such molecules ("salt or anti-polyelectrolyte effect").[25, 36-42] Thus, it can be assumed that the intriguing polymer-solubility behavior is a result of the formation of partially stable "pseudo-betaine" structures under salt-free conditions. The strong ionic attractions between the "pseudo-betaine" side groups of **6a** lead to an increase of the rigidity and therefore cause insolubility in water. While adding an excess of KBr as a foreign salt, the interactions between the side chains become less attractive and **6a** remains in solution ("salt effect"). The good solubility of **6a** in water above a critical temperature (T_c) can be explained by the release of the adamantyl carboxylate anion from the

β-CD cavity as described below. The formation of new ammonium/adamantyl carboxylate ion-pairs in the chain led to water soluble polyelectrolytes in a non-associated state.

Turbidity measurements in aqueous solution were performed to evaluate the solubility as a function of temperature (Figure 4.3). The determined clearing point of polymer complex **6a** solution appeared at 46 °C for the heating run. In accordance, the cloud point for the cooling run was observed at a temperature of 45 °C. However, the recomplexation of AdCOOK by β-CD seemed to proceed slowly within a temperature interval of approximately 40 °C in which the transmittance decreased from 100 to 0 %.

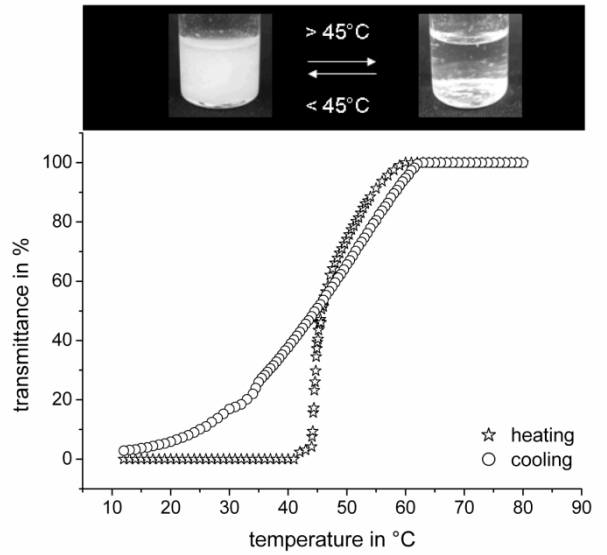


Figure 4.3 Transmittance of a 0.5 wt% aqueous solution of complexed polymer **6a** versus temperature during a heating and a cooling run.

Due to the fact that poly(pseudo-betaine) **6a** precipitates in water, the complex stability was determined in 0.1 M aqueous KBr solution by isothermal titration calorimetry. Within one experiment enthalpy, ΔH°, entropy, ΔS°, reaction stoichiometry, n, and the complex formation constant, K_s, could be obtained. Furthermore, by use of the Gibbs-Helmholtz equation the free enthalpy, ΔG°, was calculated as well. Figure 4.4 shows the heat flow as a function of time for the microcalorimetric titration at 25 °C.

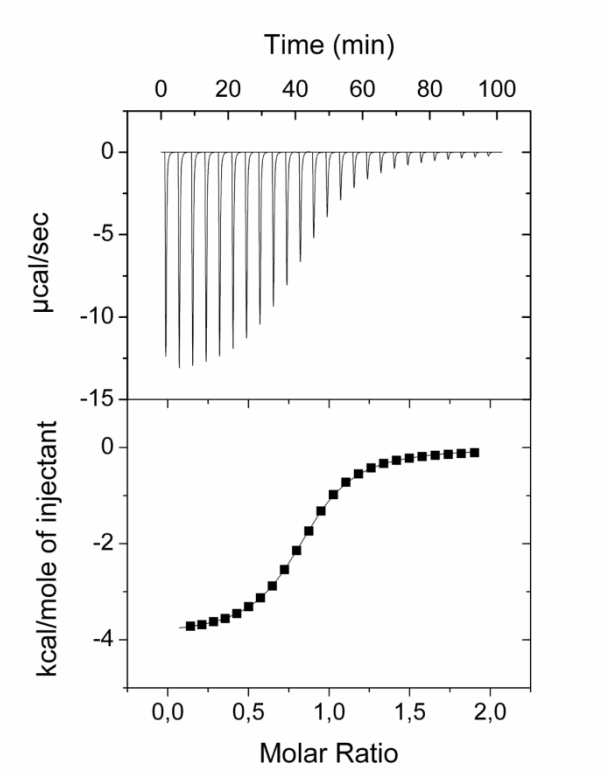


Figure 4.4 (top) Heat flow *q* as a function of time detected by a microcalorimeter upon the addition of a 10 mM solution of AdCOOK to a 1 mM solution of polymer **6** at 25 °C; (bottom) Integrated heat pulse data (quadrate symbols), corrected for dilution controls and fit (solid line) to a simple single-site binding model with parameters given in Table 4.1.

The negative heat pulses indicate exothermal complex formation. By fitting the integrated heat pulse data to a simple "one binding side" model, an excellent fit for the nonlinear regression was achieved. The estimated stability of the inclusion complex of potassium adamantyl carboxylate with the β-CD moiety of polymer **6** was relatively high (K_s = 30 500 ± 400 M^{-1}) in comparison to other guest molecules in CD chemistry, but was in the same magnitude as for native β-CD.[35] Compared to β-CD polymers described in literature, polymer **6** showed excellent binding properties.[31, 43-46]

Since the complexation process is an exothermic equilibration reaction, it strongly depends on temperature. Thus, temperature depending ITC experiments were performed (see Figure 4.6 in appendix). The obtained thermodynamic data at temperatures between 25 and 60 °C are listed in Table 4.1.

Table 4.1 Thermodynamic data for AdCOOK complexation with **6** in 0.1 M KBr solution at temperatures between 25 and 60 °C.

T [°C]	n	K_s [M^{-1}]	ΔG° [kJ/mol]	ΔH° [kJ/mol]	$T\Delta S^\circ$ [kJ/mol]
25	0.84	30 500 ± 400	-25.61	-16.39 ± 0.03	9.22
30	0.64	23 500 ± 450	-25.37	-17.20 ± 0.06	8.17
40	0.78	13 300 ± 220	-24.74	-19.63 ± 0.06	5.11
50	0.83	7 250 ± 200	-23.90	-22.38 ± 0.18	1.52
60	1.02	4 130 ± 120	-23.07	-24.13 ± 0.22	-1.06

With increasing temperature, ΔH° was more negative and the complex formation constant, K_s, decreased dramatically, whereas the value for ΔG° was nearly temperature independent. Furthermore, the positive values of TΔS° obtained for temperatures up to 40 °C were due to a substantial rearrangement and removal of water molecules originally solvated to both the cyclodextrin and the guest molecules, and further induces the release of water molecules from the cyclodextrin cavity into the aqueous KBr solution. At high temperatures (T ≥ 50°C) the change of entropy was negligible and the reaction was enthalpy driven. Summarized, with increasing temperature the complexation reaction preferably proceeded exothermic and the entropic forces were decreasing. Therefore, the complex was destabilized at higher temperatures.

In addition to the above described thermodynamic data, the molar heat capacity at constant pressure ΔC_p could be determined by temperature dependent ITC measurement as well and is defined regarding Eq. (1).

$$\Delta C_p = (\Delta H°_{T2} - \Delta H°_{T1}) / (T_2 - T_1) \quad (1)$$

Thus, ΔC_p could be calculated from the slope of a linear plot of ΔH° versus temperature (Figure 4.5). The obtained negative heat capacity changes of ΔC_p = -0.23 ± 0.01 kJ mol^{-1} K^{-1} is in the same magnitude as those reported for adamantyl carboxylate/β-CD complexation in water (pH = 7.2) of around -0.4 kJ mol^{-1} K^{-1} [47] and is well established as a thermodynamic characteristic of hydrophobic bonds.

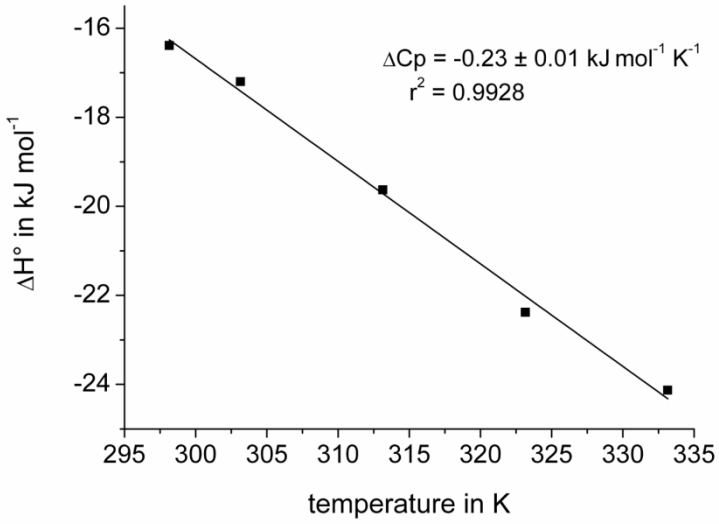


Figure 4.5 Temperature dependence of enthalpy ΔH°. ΔC_p was determined from the slope of linear regression (solid line).

4.3 Conclusion

The experiments and results clearly show that the investigated system of β-CD modified polyelectrolyte **6** and potassium adamantyl carboxylate reveals new opportunities in the field of thermosensitive systems based on non-covalent host/guest interactions. For the first time the formation of a "pseudo-betaine" structure was observed by non-covalent interactions between a CD-containing polyelectrolyte as host and adamantyl carboxylate as a guest. The discovered reversible UCST behavior in aqueous solution was due to a physical cross-linking by cooperative hydrophobic and ionic interactions. At higher temperatures adamantyl carboxylate is released from the CD-moiety and the polymer redissolved.

4.4 Experimental Details

4.4.1 Materials

β-Cyclodextrin (β-CD) was obtained from Wacker-Chemie GmbH (Burghausen, Germany). Prior to use, β-CD was dried in a CEM Sam 255 microwave drying system and stored in a desiccator under vacuum over sicapent.

N,*N*-dimethylaminoethyl methacrylate (98 %, inhibited with 2000ppm HEHQ) and azobisisobutyronitrile (98 %) were obtained from Aldrich Chemicals (Germany) and propargyl bromide (80 wt%-solution in toluene) was obtained from Acros Organics (Belgium). Sodium azide (99 %) was purchased from Honeywell Riedel de Haën® (Germany) and copper(II) sulfate pentahydrate (>99 %) was obtained from Fluka (Germany). Sodium L(+)-ascorbate (99 %) was obtained from AppliChem (Germany). Dimethylsulfoxide-d_6 99.8 atom % D was purchased from Eurisotop® (France). Dialysis membranes with a molecular weight cut off (MWCO) of 3.5 kDa were obtained from Spectra/Por, Germany. All commercially available reagents and solvents were used without further purification.

4.4.2 Measurements and Methods

The structures of the synthesized monomers and polymers were proven by ^{1}H- and ^{13}C-NMR spectroscopy using a Bruker Avance DRX 500 spectrometer at 500.13 MHz for proton and 125.77 MHz for carbon. Using DMSO-d_6 as solvent, chemical shifts were referenced to the solvent value at δ_H = 2.51 ppm and δ_C = 39.52 ppm, respectively. All samples were measured at room temperature.

C, H, N - elemental composition analysis was determined using a Perkin Elmer 2400 CHN analyzer.

Infrared spectra were recorded on a Nicolet 6700 FT-IR spectrometer equipped with a diamond single bounce ATR accessory at room temperature.

Melting points were determined at a Büchi meting point B-545 instrument.

MALDI-TOF-MS was performed on a Bruker Ultraflex time-of-flight mass spectrometer using a 337 nm nitrogen laser. 2,5 Dihydroxybenzoic acid (DHB) was used as sample matrix.

Electrospray ionization (ESI) mass spectrometry was carried out on a Finnigan LCQ Deca Ion-Trap-API mass spectrometer.

Molar mass distributions measurements were carried out at 25 °C using the commercial aFFFF-System Eclipse 2 (Wyatt Technology Europe, WTE, Dernbach, Germany). The eluent flow was provided by a solvent reservoir, an on-line degasser, isocratic pump, and auto injector (Agilent 1200 series). A short channel equipped with polyethersulfonate membrane (MWCO 10 kDa, WTE) and a 250 µm spacer (WTE, type wide) was used. Thirty microliters of the sample solution (c = 1 mg ml^{-1}) was injected into the channel. The separations were

carried out using an elution profile with a flow rate V=1.0 ml min^{-1} and an ambient cross-flow. The outlet of eclipse 2 was connected to the miniDAWN treos three-angle light scattering photometer followed by an Optilab rEX dRI detector. Eluent was 0.1 M aqueous potassium bromide solution with 500 ppm sodium azide at a flow rate 1ml/min. Molecular weight was calculated with Astra5 software from static light scattering data, using Zimm-model. As concentration source, refractive index was used. Calibration of the system was performed by bovin serum albumin.

Turbidity measurements were determined using a TP1 turbidity photometer from Tepper over a temperature range of 10 to 80 °C. 0.015 g of the polymer and an equimolar amount of potassium adamantyl carboxylate was dissolved in 2985 µl of water. During continuous stirring, the transparency of the sample was determined by a voltage controlled semiconductor laser and a silicon photodiode at a wavelength of 500 nm and a heating or cooling rate of 1 °C min^{-1}. All critical temperatures were detected by determination of the temperature where the transparency of the solution was increased to 50 % of the initial value.

Microcalorimetric titrations were accomplished with an isothermal calorimeter of type VP-ITC from MicroCal. 0.1 M aqueous potassium bromide solution was used for the solutions of the host and guest. The concentration of the host solution was 1 mmol l^{-1} and the concentration of the guest solution was 10 mmol l^{-1}. In the experimental process the guest solution in the syringe was placed over 25 or 30 injections with a respective volume of 10 µl into the measuring cell, which was filled with the host solution. During the measurement the solution was stirred at a rotational speed of 300 min^{-1}. Each injection was made over a period of 20 s, whereas the time between two injections was 4 and 6 min, respectively. The dilution heat was determined in a separate measurement by injection of the guest in 0.1 M aqueous potassium bromide solution and subtracting it from the determined heat flow. The evaluation of the received data was carried out with a MicroCal LLC ITC add-on modified version of the software Origin7. Since the released complex formation heat is directly proportional to the amount of binding, it was monitored over time. By integration of each peak, correction of the cell volume and, sample concentration, the binding isotherm was obtained. It was fitted by a least square fit (LSF), whereas Eq. (2) regards the number of independent binding sites. The enthalpy change, ΔH, the binding constant, K, and the reaction stoichiometry, n, are adjustable parameters.

$$Q = \frac{n \cdot M_t \cdot V\Delta H}{2} \cdot \left[\left(1 + \frac{1}{n \cdot M_t \cdot K} + \frac{X_t}{n \cdot M_t} \right) - \sqrt{\left(1 + \frac{1}{n \cdot M_t \cdot K} + \frac{X_t}{n \cdot M_t} \right)^2 - \frac{4 \cdot X_t}{n \cdot M_t}} \right] \quad (2)$$

Furthermore, Q is the heat change, K the binding constant, n the number of sites / reaction stoichiometry, V the active cell volume, M_t the total concentration of host, and X_t the total concentration of guest.

Excellent results could be obtained by "one binding side" approximation, although complexation reactions with cyclodextrin moieties at a polymer chain are not truly independent.

4.4.3 Monomer syntheses

***N*, *N*-dimethyl-[2-(2-methyl-acryloyloxy)-ethyl]-prop-2-ynyl-ammonium bromide, 3**

The monomer was synthesized by mixing N, N-dimethylaminoethyl methacrylate **1** (5 g, 0.032 mol) and a slightly excess of propagyl bromide **2** (0.035 mol, 80 wt%-solution in toluene) in a 50 ml flask. The mixture was stirred under nitrogen atmosphere overnight. Subsequent the raw product was diluted with acetone, filtered off, washed several times with diethyl ether and dried under vacuum to yield 7.4 g (86 %) of a white solid.

mp. ~134°C

IR (cm^{-1}) 3183, 3013, 2965 (CH_2, CH_3); 2123 (C≡C); 1726 (C=O); 1640 (C=C); 1159 (CO)

^{1}H NMR δ/ppm (500 MHz, DMSO-d_6) = 6.11 (s, 1H, C**H$_2$**=C(CH_3)-); 5.77 (s, 1H, C**H$_2$**=C(CH_3)-); 4.60 (m, 2H, -O-C**H$_2$**-); 4.55 (m, 2H, -N^+(CH_3)$_2$-C**H$_2$**-); 4.12 (s, 1H, -C≡C**H**); 3.82 (m, 2H, -O-CH_2C**H$_2$**-); 3.21 (s, 6H, -N^+(C**H$_3$**)$_2$-); 1.92 (s, 3H, CH_2=C(C**H$_3$**)-)

^{13}C NMR δ/ppm (125 MHz, DMSO-d_6) = 166.23 (-**C**OO-); 135.71 (CH_2=**C**(CH_3)); 127.09 (**C**H_2=C(CH_3)-); 83.60 (-C≡**C**H); 72.74 (-**C**≡CH); 62.17 (-**C**H_2-N^+(CH_3)$_2$-); 58.52 (-O-**C**H_2-); 54.52 (-**C**H_2-C≡CH); 50.64 (-N^+(**C**H_3)$_2$-); 16.30 (CH_2=C(**C**H_3)-)

MS-ESI *m/z* = 196.3 (64 %) [M^+], 129.1 (70 %), 113.1 (100 %)

C, H, N $C_{11}H_{18}BrNO_2$ (275.05 g mol^{-1})

calc. (%):	C: 47.84	H: 6.57	N: 5.07
found (%):	C: 47.78	H: 6.43	N: 5.08

Mono-6-azido-6-deoxy-β -cyclodextrin, 4

Mono-6-azido-6-deoxy-β-cyclodextrin **4** was prepared according to a method described in literature.[48] The product was obtained as a white solid in 78 % yield.

MALDI-tof *m/z* = 1182.4 [M+Na]$^+$

IR (cm^{-1}) 3316 (OH); 2924 (CH); 2103 (N_3); 1364, 1152 (C-O-C); 1077 (OH); 1025 (C-O)

^{1}H NMR δ/ppm (500 MHz, DMSO-d_6) = the * notation refers to the glucose unit bearing the azide group; 5.73 (m, 14H, $OH_{2,3}$); 4.92 (d, $^3J_{H,H}$ = 3.15 Hz, 1H, H_1*); 4.85 (d, $^3J_{H,H}$ = 3.15 Hz, 6H, H_1); 4.60-4.44 (br.m, 6H, OH_6); 3.84-3.60 (br.m, 28H, $H_{3,5,6}$); 3.32 (m, 14H, $H_{2,4}$)

^{13}C NMR δ/ppm (125 MHz, DMSO-d_6) = the * notation refers to the glucose unit bearing the azide group; 102.63, 102.39, 101.95 (C_1); 83.34 (C_4*); 82.23, 81.90, 81.75 (C_4); 73.41, 73.24 (C_3); 72.77, 72.55, 72.39 (C_2, C_5); 70.55 (C_5*); 60.50, 60.28 (C_6); 51.45 (C_6*)

C, H, N $C_{42}H_{69}N_3O_{34}$ (1160 g mol^{-1})

calc. (%):	C: 43.49	H: 6.00	N: 3.62
found (%):	C: 42.13	H: 6.24	N: 3.42

Monofunctional β-CD monomer 5

N,N-dimethyl-[2-(2-methyl-acryloyloxy)-ethyl]-prop-2-ynyl-ammonium bromide **3** (552 mg, 2 mmol) was added to a solution of mono-6-azido-6-deoxy-β-cyclodextrin **4** (2.32 g, 2 mmol) in H_2O (20 ml). In presence of Cu(I) generated in situ by the reduction of copper(II) sulfate pentahydrate (25 mg, 0.1 mmol) with sodium-L-(+)-ascorbate (39.6 mg, 0.2 mmol), the reaction mixture was stirred at 100°C overnight. After adding pentaerythrit-tetrakis-(3-mercapto-propionat) (49 mg, 0.1 mmol) the solution was filtered and precipitated into acetone. The collected product was dried under vacuum, redissolved in water and freeze dried to give 2.51 g (1.75 mmol, 87 %) of a white solid.

MALDI-tof *m/z* = 1355.51 $[M]^+$

C, H, N $C_{53}H_{87}BrN_4O_{36}\cdot 4H_2O$ (1508.23 g mol^{-1})

calc. (%):	C: 42.21	H: 6.35	N: 3.71
found (%):	C: 42.28	H: 6.52	N: 3.16

IR (cm^{-1}) 3305 (OH); 2926 (CH_2, CH_3); 1720 (C=O); 1654 (C=C); 1152 (C-O-C); 1078 (OH); 1027 (C-O)

^{1}H NMR δ/ppm (500 MHz, DMSO-d_6) = the * notation refers to the glucose unit bearing the azide group; 8.37 (s, 1H, $H_{triazol}$); 6.11 (s, 1H, C**H_2**=C(CH_3)-); 5.91-5.61 (br(m), 15H, $OH_{2,3}$-CD, C**H_2**=C(CH_3)-); 5.05 (s, 1H, H_1*-CD), 4.84 (br(s), 12H, H_1-CD, OH_6-CD); 4.75 (br, 2H, -O-C**H_2**-), 4.60 (br, 2H, -N^+(CH_3)$_2$C**H_2**-) 3.99 (m, 2H, -O-CH_2C**H_2**-); 3.64 (br(m), 28H, $H_{3,5,6}$-CD); 3.35 (br(m), 14H, $H_{2,4}$-CD); 3.09 (s, 6H, -N^+(C**H_3**)$_2$-); 1.92 (s, 3H, CH_2=C(C**H_3**)-)

^{13}C NMR δ/ppm (125 MHz, DMSO-d_6) = the * notation refers to the glucose unit bearing the azide group; 166.27 (-**C**OO-); 135.74 (CH_2=**C**(CH_3)-), 130.24, 129.77 (**C**, **C**H -triazol); 127.07 (**C**H_2=C(CH_3)-); 102.46, 102.29, 101.86 (**C**$_1$-CD); 83.73 (**C***$_4$-CD); 82.25, 81.89, 81.64 (**C**$_4$-CD); 73.58, 73.40 (**C**$_3$-CD); 72.77, 72.52, 72.39 (**C**$_2$, **C**$_5$ -CD); 70.60 (**C***$_5$-CD); 62.09 (-**C**H_2-N^+(CH_3)$_2$-); 60.41, 60.27 (**C**$_6$-CD), 59.58 (-CH_2CH_2-N^+(CH_3)2-CH2-); 58.55 (-O-**C**H_2CH_2-), 50.42 (-N^+(**C**H_3)$_2$-); 18.31 (CH_2=C(**C**H_3)-)

4.4.4 Polymerization

Polymer 6

1g (0.69 mmol) of **5** was dissolved in DMF (4 ml). After purging the solution with nitrogen for 20 min, AIBN (1.14 mg, 1 mol-% = 0.069 mmol) was added as a radical initiator and the solution was stirred at 60 °C (oil bath) overnight. Afterwards, it was subsequently precipitated in acetone and the crude product was collected by filtration. Purification by dialysis (in water, MWCO = 3.5 kDa, 3d, RT) and freeze drying yielded polymer **6**.

M_n 59 kDa, PD 1.4

^{1}H NMR δ/ppm (500 MHz, DMSO-d_6) = 8.53 (br, 1H, **H** triazol); 5.09 (br (m), 7H, H_1-CD); 4.60 (br, 4H, -C**H_2**CH_2-N^+(CH_3)$_2$-C**H_2**-); 4.27 (br, 2H, -O-CH_2C**H_2**-); 4.16 - 3.04 (br (m), 48H, $H_{2,3,4,5,6}$-CD, OH_6-CD); 2.29 - 1.89 (br, 2H, backbone C**H_2**); 1.55 - 0.88 (br, 3H, backbone C**H_3**)

IR (cm^{-1}) 3329 (OH); 2926 (CH_2, CH_3); 1728 (C=O); 1151 (C-O-C); 1078 (OH); 1027 (C-O)

C, H, N $[C_{53}H_{87}BrN_4O_{36}\cdot 7H_2O]$

[calc. (%):	C: 40.75	H: 6.52	N: 3.59]
found (%):	C: 40.95	H: 6.64	N: 3.83

4.5 References

[1] V. V. Rostovstev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Ang. Chem. Int. Ed.* **2002**, *41*, 2596.

[2] C. W. Tornøe, C. Christensen, M. Meldal, *J. Org. Chem.* **2002**, *67*, 3057.

[3] C. W. Tornøe, M. Meldal, *Chemical Reviews* **2008**, *108*, 2952.

[4] D. D. Díaz, S. Punna, P. Holzer, A. K. McPherson, K. B. Sharpless, V. V. Fokin, M. G. Finn, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4392.

[5] A. J. Scheel, H. Komber, B. I. Voit, *Macromol. Rapid. Commum.* **2004**, *25*, 1175.

[6] B. Helms, J. L. Mynar, C. J. Hawker, J. M. J. Frechet, *J. Am. Chem. Soc.* **2004**, *126*, 15020.

[7] W. H. Binder, C. Kluger, *Macromolecules* **2004**, *37*, 9321.

[8] N. V. Tsarevsky, K. V. Bernaerst, B. Dufour, F. E. DuPrez, K. Matyjaszewski, *Macromolecules* **2004**, *37*, 9308.

[9] M. Munteanu, S. Choi, H. Ritter, *Macromolecules* **2008**, *41*, 9619.

[10] T. Trellenkamp, H. Ritter, *Macromolecules* **2010**, *43*, 5538.

[11] H. Feil, Y. H. Bae, J. Feijen, S. W. Kim, *Macromolecules* **1993**, *26*, 2496.

[12] J. Zhang, N. A. Peppas, *Macromolecules* **2000**, *33*, 102.

[13] H.-C. Chin, Y.-F. Lin, S.-H. Hung, *Macromolecules* **2002**, *35*, 5235.

[14] L. D. Taylor, L. D. Cerankowski, *J. Polym. Sci. Polym. Chem. Ed.* **1975**, *13*, 2551.

[15] T. Trellenkamp, H. Ritter, *Macromol. Rapid Commun*. **2009**, *30*, 1736.

[16] S. Schmitz, H. Ritter, *Angew. Chem. Int. Ed.* **2005**, *44*, 5658.

[17] O. Kretschmann, C. Steffens, H. Ritter, *Angew. Chem. Int. Ed.* **2007**, *46*, 1.

[18] O. Kretschmann, S. W. Choi, M. Miyauchi, I. Tomatsu, A. Harada, H. Ritter, *Angew. Chem. Int. Ed.* **2006**, *45*, 4361.

[19] S. Schmitz, H. Ritter, *Macromol. Rapid Commun.* **2007**, *28*, 2080.

[20] H. Katono, K. Sanui, N. Ogata, T. Okano, Y. Sakurai, *Polymer J.* **1991**, *23*, 1179.

[21] H. Katono, A. Maruyama, K. Sanui, N. Ogata, T. Okano, Y. Sakurai, *J. Controlled Release*, **1991**, *16*, 215.

[22] H. Sasase, T. Aoki, H. Katono, K. Sanui, N. Ogata, R. Ohta, T. Kondo, T. Okano, and Y. Sakurai, *Makromol. Chem. Rapid Commun.* **1992**, *13*, 577.

[23] H. S. Choi, T. Ooya, S. Sasaki, N. Yui, *Macromolecules* **2003**, *36*, 5342.

[24] O. Azzaroni, A. A. Brown, W. T. S. Huck, *Angew. Chem.* **2006**, *118*, 1802.

[25] H. Ladenheim, H. Morawetz, *J. Polym. Sci.* **1957**, *26*, 251.

[26] R. Hart, D. Timmerman, *J. Polym. Sci.* **1958**, *28*, 638.

[27] A. B. Lowe, C. L. McCormick, *Chem. Rev.* **2002**, *102*, 4177.

[28] A. V. Dobrynin, R. H. Colby, M. Rubinstein, *J. Polym. Sci., Part B* **2004**, *42*, 3513.

[29] S. Kudaibergenov, W. Jaeger, A. Laschewsky, *Adv. Polym. Sci.* **2006**, *201*, 157.

[30] S. Choi, M. Munteanu, H. Ritter, *J. Polym. Res.* **2009**, *16*, 389.

[31] S. Amajjahe, S. Choi, M. Munteanu, H.Ritter, *Angew. Chem. Int. Ed.* **2008**, *47*, 3435.

[32] M. Furue, A. Harada, S. I. Nozakura, *J. Polym. Sci. Part C* **1975**, *13*, 357.

[33] A. Harada, M. Furue, S. Nozakura, *Macromolecules* **1976**, *9*, 701.

[34] J. Wang, M. Jiang, *J. Am. Chem. Soc.* **2006**, *128*, 7639.

[35] M. V. Rekharsky, Y. Inoue, *Chem. Rev.* **1998**, *98*, 1875.

[36] J. C. Salamone, W. Volksen, A. P. Olson, S. C. Israel, *Polymer* **1978**, *19*, 1157.

[37] D. N. Schulz, D. G. Peiffer, P. K. Agarwal, J. Larabee, J. J. Kaladas, L. Soni, B. Handwerker, R. T. Garner, *Polymer* **1986**, *27*, 1734.

[38] A. Z. Niu, D. J. Liaw, H. C. Sang, C. Wu, *Macromolecules* **2000**, *33*, 3492.

[39] P. Mary, D. D. Bendejacq, M. P. Labeau, P. Dupuis, *J. Phys. Chem. B* **2007**, *111*, 7767.

[40] Y. M. Park, *Commun. Math. Phy*. **1979**, *70*, 161.

[41] G. D. J. Phillies, *J. Chem. Phys.* **1974**, *60*, 2721.

[42] R. Kumar, G. H. Fredrickson, *J. Chem. Phys*. **2009**, *131*, 104901.

[43] V. Wintgens, S. Daoud-Mahammed, R. Gref, L. Bouteiller, C. Amiel, *Biomacromolecules* **2008**, *9*, 1434.

[44] T. Terndrup Nielsen, V. Wintgens, K. Lambertsen Larsen, C. Amiel, *J. Incl. Phenom. Macrocycl. Chem.* **2009**, *65*, 341.

[45] M. E. Martínez Barbosa, L. Bouteiller, S. Cammas-Marion, V. Montembault, L. Fontaine, G. Ponchel, *J. Mol. Recognit.* **2008**, *21*, 169.

[46] A. Charlot, R. Auzély-Velty, *Macromolecules* **2007**, *40*, 1147.

[47] J. C. Harrison, M. R. Eftink, *Biopolymers* **1982**, *21*, 1153.

[48] K. Ohga, Y. Takashima, H. Takahashi, Y. Kawaguchi, H. Yamaguchi, A. Harada, *Macromolecules* **2005**, 38, 5897.

4.6 Appendix

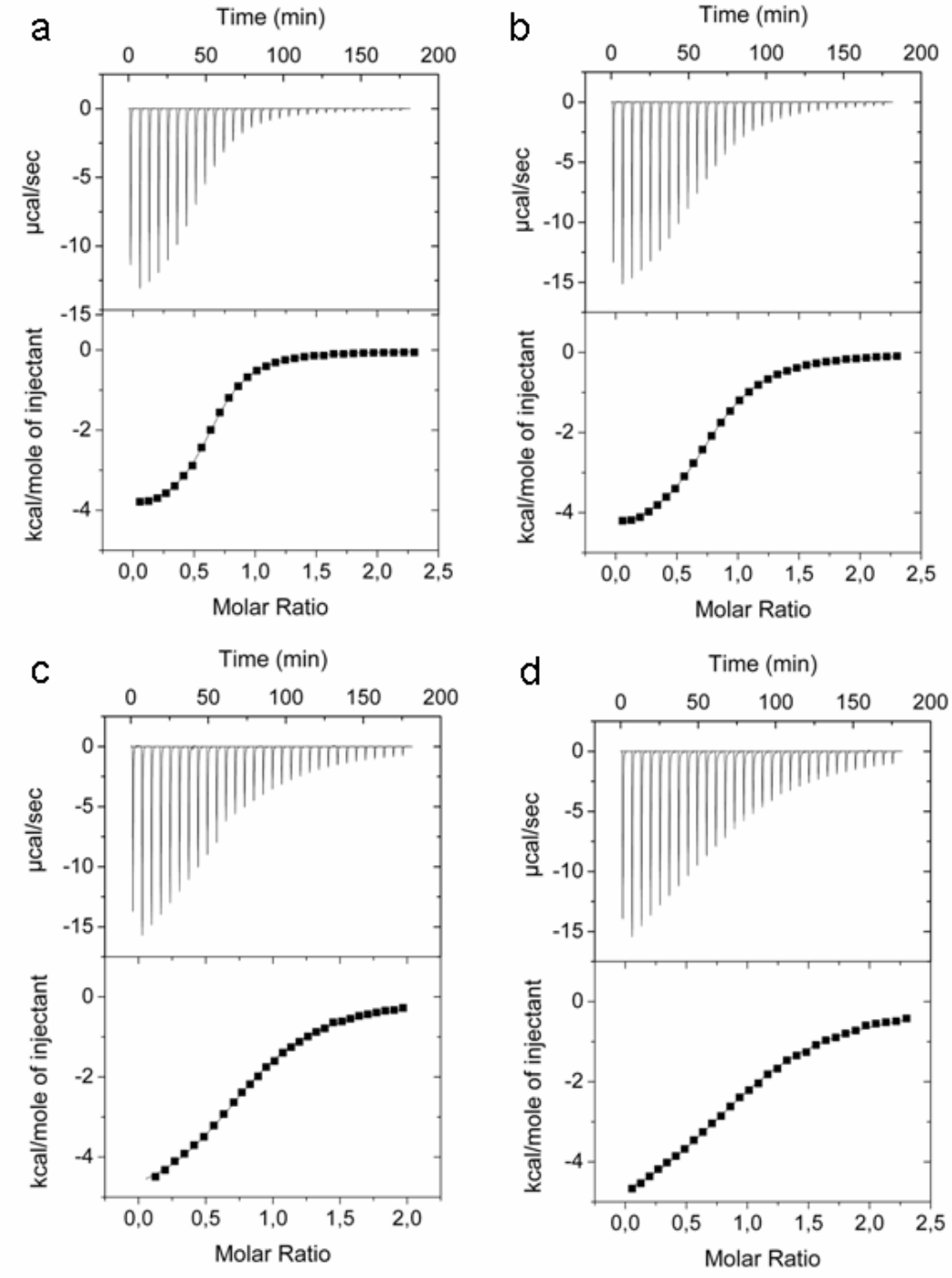
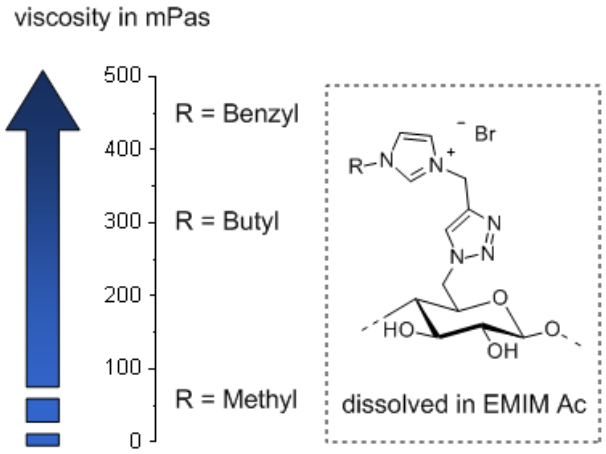


Figure 4.6 Final ITC figures for the addition of a 10 mM solution of AdCOOK to a 1 mM solution of polymer **6** at a) 30°C, b) 40°C, c) 50°C, d) 60°C.

Chapter 5

Novel Polyelectrolytes Based on Cellulose and Ionic Liquids



Abstract

The regioselective derivatization of cellulose with three different ionic liquids via click chemistry was investigated. The obtained polyelectrolytes were characterized in detail by elemental analysis, FT-IR-spectroscopy, ^{1}H and ^{13}C NMR spectroscopy. In addition, the rheological behavior of the cellulose samples was studied in 1-ethyl-3-methyl imidazolium acetate as solvent. A Newtonian flow behavior was recorded for all cellulose samples at a concentration of 5 wt%. Due to the modification, the viscosity was reduced by at least one decade compared to unmodified cellulose and could be controlled by choice of the substituent of the imidazolium ring. Furthermore, the viscosity-temperature dependence was analyzed with the Vogel-Fulcher-Tammann equation and the Arrhenius plot, respectively.

Parts of this chapter will be published: N. Gonsior, H. Ritter, submitted.

5 Polyelectrolytes Based on Cellulose and Ionic Liquids

5.1 Introduction

In the field of sustainable chemistry, polysaccharides are remarkable raw materials for defined modifications and specific applications.[1] In particular cellulose and its derivatives are promising alternatives to products derived from petrochemical industry. They are already utilized in various fields, e.g. material science, pharmaceutics, "green" chemistry, and nutrition supplements. The most important cellulose-based polyelectrolyte is carboxymethyl cellulose (CMC), which is used for controlling the viscosity and texture of aqueous mixtures. It is produced in large quantities by etherification of alkali cellulose with chloroacetic acid.[2] Besides esterification, this reaction is the most common approach for modification of polysaccharides. But the similar reactivity of the three hydroxyl groups of the anhydroglucose unit (AGU) towards electrophiles results in a statistic functionalization pattern.[1] However, regioselective modification is essential to obtain new structures and properties for cellulose based materials.

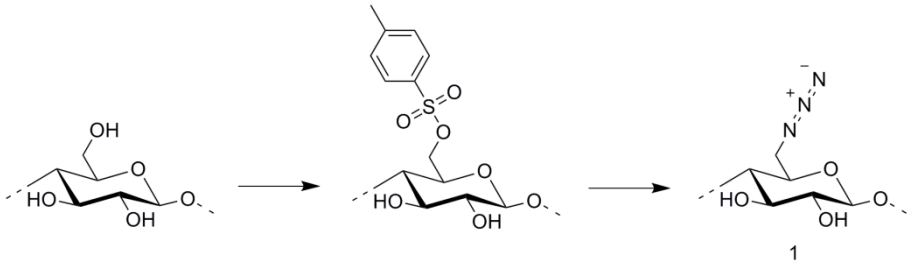
Recently, the copper(I) catalyzed azide/alkyne click reaction (CuAAc), introduced by Sharpless and Meldal independently in 2002,[3,4] has been proven to be an appropriate modification strategy for cellulose. In contrast to polysaccharide esterification, no cross-linking occurred and hydrolytically stable products could be obtained.[5] The wide scope of acceptable functional groups and solvents, the mild reaction conditions, high yield and high degree of substitution are further benefits for polysaccharide modification via click chemistry. Therefore, multifunctional cellulose materials were obtained via click chemistry by the regioselective introduction of various compounds, e.g. methylcarboxylate, 2-aniline, and 3-thiophene moieties,[5] sugar residues,[6] fluorophores,[7] dendrons,[8] as well as anionic,[9] and cationic[10] moieties. Furthermore, nanoplatelet gels and hydrogels could be obtained by chemical cross-linking of azide and alkyne bearing cellulose derivates via click chemistry.[11-13]

However, for the processing and chemical derivatization the dissolution of cellulose is essential. In this context, ionic liquids (ILs) have been suggested as promising cellulose solvents. Especially, in imidazolium based ILs like 1-ethyl-3-methyl imidazolium acetate [EMIM][Ac] or 1-butyl-3-methyl imidazolium chloride [BMIM][Cl], cellulose can be dissolved in rather high concentrations without any preactivation.[14] In addition, the rheological properties of cellulose/IL solutions have been described in detail in literature.[14-19]

In this chapter, the synthesis of novel polyelectrolytes based on cellulose and ionic liquids via click chemistry is presented. Furthermore, the rheological behavior of the obtained cellulose derivatives dissolved in [EMIM][Ac] was analyzed regarding the influence of the substituents.

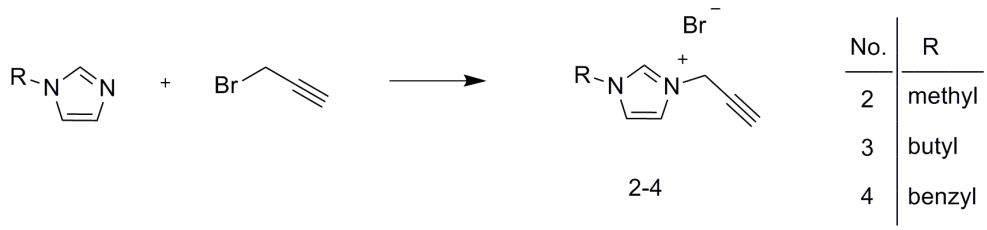
5.2 Results and Discussion

Azide-modified cellulose was synthesized and purified according to literature.[5,20] Based on cellulose tosylate a homogeneous nucleophilic displacement reaction in DMF with sodium azide led to 6-azido-6-desoxy cellulose (**1**) with a DS value of 1.01 (Scheme 5.1). The FT-IR spectrum of **1** showed a characteristic signal at 2103 cm^{-1} for the azide moiety and further the νSO_2 bands of the tosyl moiety at 1356 cm^{-1} and 1172 cm^{-1} disappeared.



Scheme 5.1 Reaction scheme for the preparation of 6-azido-6-desoxy cellulose (**1**) according to literature.[5,20]

Furthermore, the copper(I) catalyzed azide/alkyne click reaction (CuAAc) of **1** with alkyne containing ionic liquids (ILs) was investigated. Therefore, propargyl bromide was added in a small excess to three different imidazole derivatives to obtain 1-alkyl/benzyl-3-propargyl imidazolium bromide (**2**-**4**) compounds (Scheme 5.2) with yields between 66 % and 86 %. 1-Methyl-3-propargyl imidazolium bromide (**2**) was obtained as a white solid with a melting point around 70 °C, whereas 1-butyl-3-propargyl imidazolium (**3**) and 1-benzyl-3-propargyl imidazolium bromide were liquid at room temperature and slightly yellow. The color was thought to originate from impurities of the educts, since they were used as received. All ILs were confirmed by NMR and IR spectroscopy, as well as elemental analysis.



No.	R
2	methyl
3	butyl
4	benzyl

Scheme 5.2 Synthesis of propargyl containing imidazolium derivatives **2**-**4**.

The ^{1}H-NMR spectra of **2** to **4** are depicted in Figure 5.1. The significant peak for the alkyne proton appeared at approximately 3.9 ppm for all ILs (**2**-**4**). Furthermore, the imidazolium proton peak of N(1)CHN(3) was observed at 9.31 ppm (**2**), 9.51 ppm (**3**) and 9.63 ppm (**4**), respectively. Due to the increasing hydrophobicity of the imidazolium substituents (**2** < **3** < **4**), the proton peak was downfield shifted.

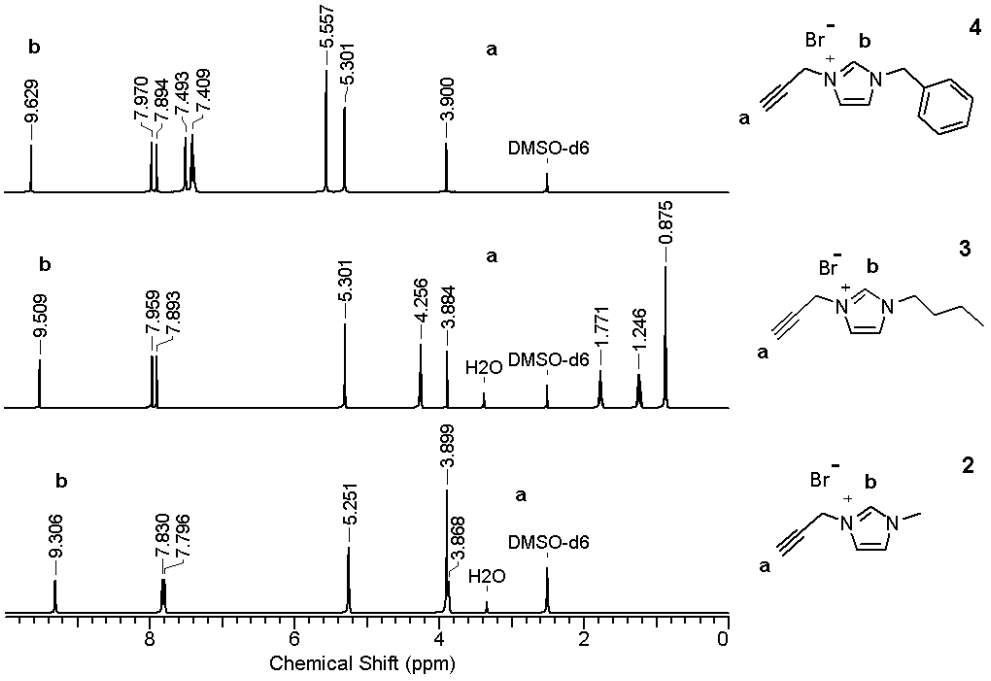
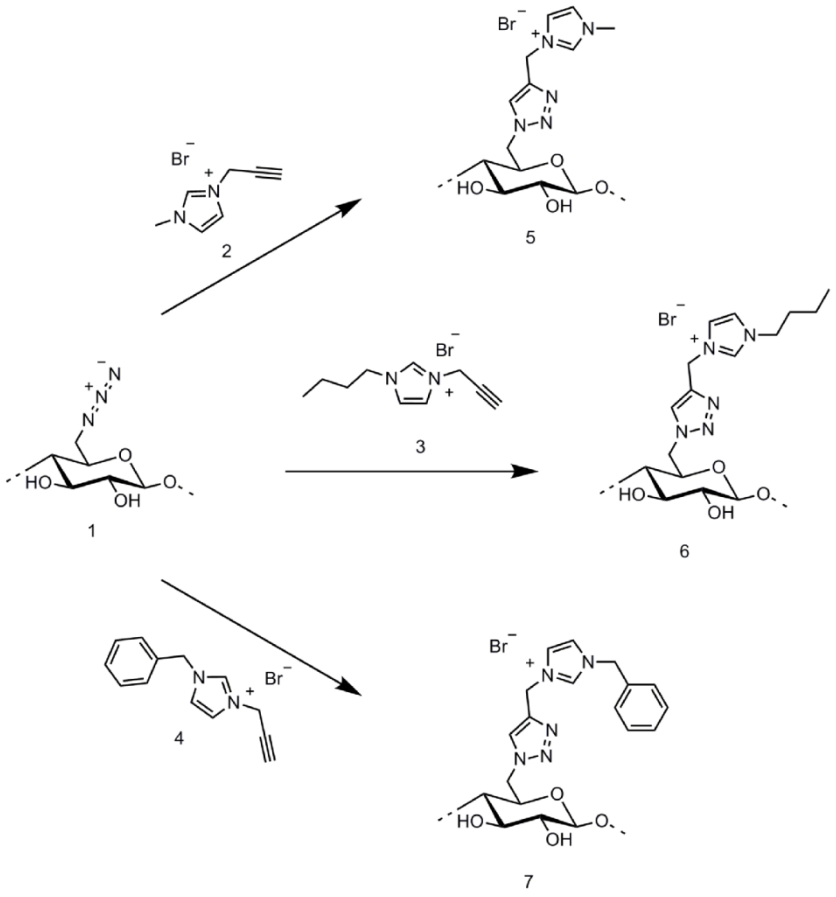


Figure 5.1 ^{1}H-NMR spectra of 1-alkyl/benzyl-3-imidazolium bromide **2**, **3**, and **4**.

The chemical regioselective modification of 6-azido-6-desoxy cellulose (**1**) with ILs (**2**-**4**) was achieved by CuAAc reaction in DMSO at ambient temperature to give new water soluble polyelectrolytes **5**, **6**, and **7** (Scheme 5.3). The active copper (I) catalytic species was generated in situ by reduction of $CuSO_4$ with sodium ascorbate.[3,4]



Scheme 5.3 Synthesis of cellulose derivatives (**5**-**7**) via CuAAc reaction.

^{13}C-NMR spectroscopy of **5**, **6**, and **7** confirmed the successful progress of the click reaction and showed no impurities or substructures resulting from side reactions. In case of 1-methylimidazolium bromide functionalized cellulose (**5**) linked by a 1,4-disubstituted 1,2,3-triazole, the characteristic peaks of imidazolium appeared at 136.9, 124.2, and 122.6 ppm (Figure 5.2, top). The peaks of the C-atoms of the triazole moiety were shown at 140.4 and 126.7 ppm, respectively. Furthermore, signals for the carbons of AGU were found at 50.8 ppm for C_6, 70.6-79.7 ppm for C_2-C_5 and 102.7 ppm for C_1.

The spectrum of 1-butylimidazolim bromide modified cellulose (**6**) contained all above described significant peaks, but also signals for the butyl group in the range from 12.8 to 48.5 ppm (Figure 5.2, below).

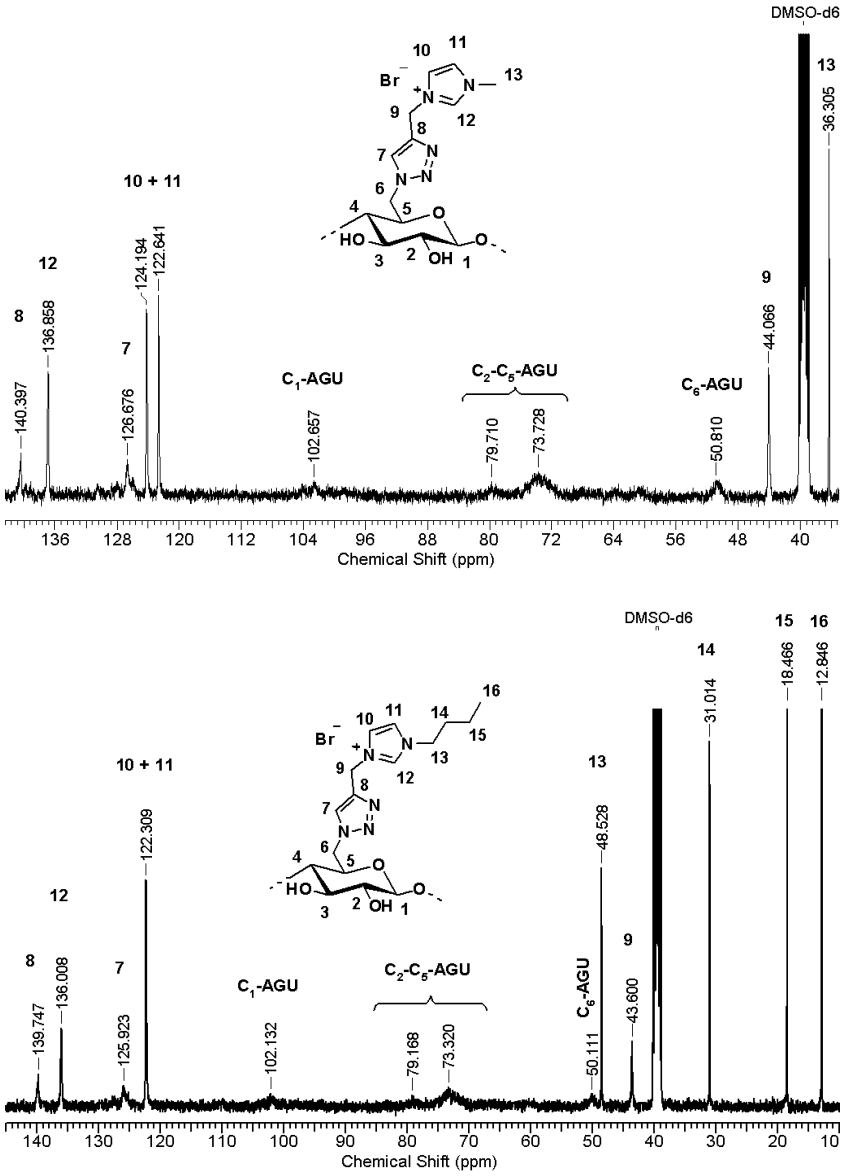


Figure 5.2 ^{13}C-NMR spectra of **5** (top) and **6** (below), respectively.

The ^{1}H-NMR and ^{13}C-NMR spectra for 1-benzylimidazolim bromide functionalized cellulose (**7**) are shown in Figure 5.3. The signals for all structural features were found in the ^{1}H-NMR spectrum, e.g. at 8.5 ppm for the triazole proton, at 5.14-2.85 ppm for the AGU protons, and at around 7.4 ppm for the phenyl protons. Moreover, also the ^{13}C-NMR spectrum confirmed

the structure. The aromatic carbon signals appeared at 135.0 ppm and between 129.4 to 128.9 ppm, respectively.

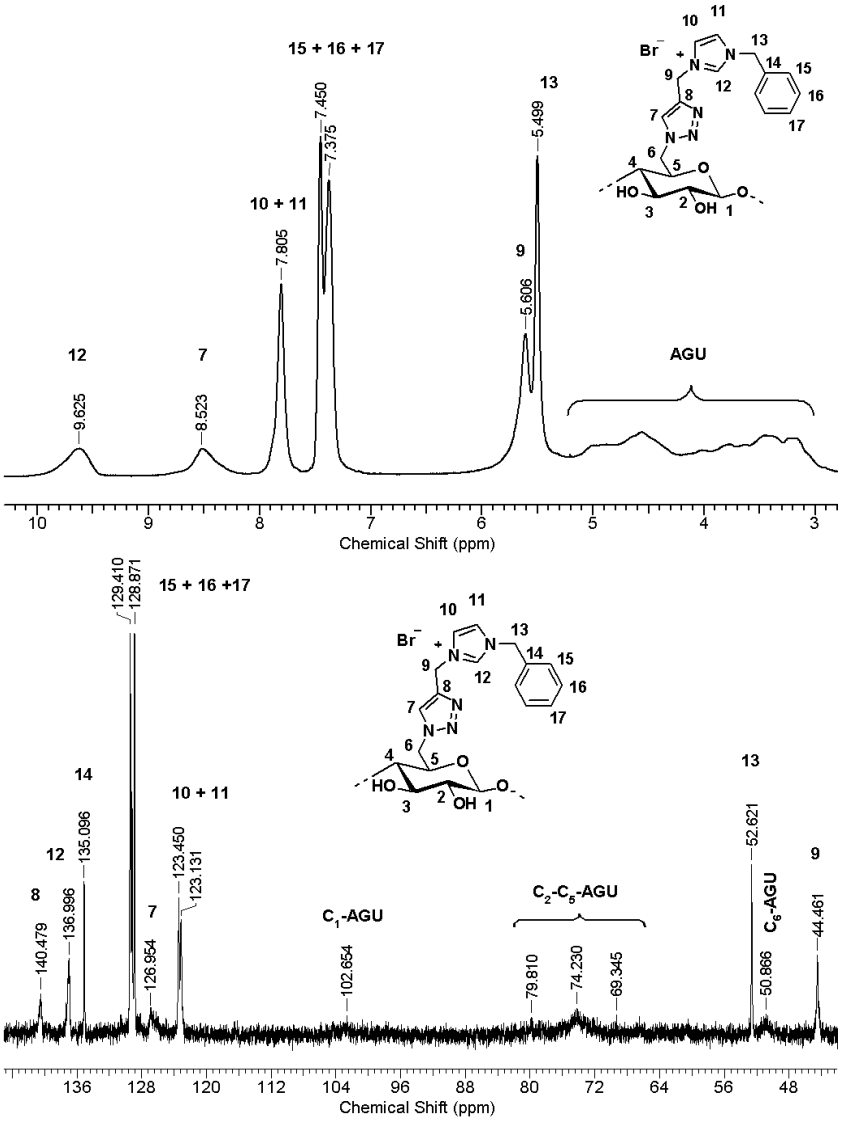


Figure 5.3 ^{1}H-NMR (top) and ^{13}C-NMR (below) spectrum of 1-benzylimidazolium bromide functionalized cellulose (**7**) linked by a 1,4-disubstituted 1,2,3-triazole.

Furthermore, the degree of substitution (DS) values of the obtained celluloses samples **5** to **7** were calculated form the N-content determined by elemental analysis and were 0.98 (**5**), 0.99 (**6**), and 0.97 (**7**), respectively. Therefore, nearly all repeating units were modified with an ionic moiety at C_6-position of the AGU.

Due to the modification with ionic groups, cellulose derivatives **5**-**7** were soluble in water, DMSO and 1-ethyl-3methyl imidazolium acetate [EMIM][Ac], but insoluble in DMF. Table 5.1 summarizes the DS values and the solubility properties of **5**-**7** as well.

Table 5.1 DS values and solubilities of ionic liquid modified celluloses[a].

No.	DS	solvent						
	EA[b]	H_2O	Acetone	DMSO	DMF	THF	CH2Cl2	[EMIM][Ac]
5	0.98	✓	x	✓	x	x	x	✓
6	0.99	✓	x	✓	x	x	x	✓
7	0.97	✓	s	✓	x	s	x	✓

[a] ✓-soluble at room temperature, x -insoluble, s -swellable at a concentration of 1 g / 100 ml;
[b] calculated from N-content determined by elemental analysis

The rheological properties of pure cellulose dissolved in ionic liquids have been studied extensively.[14-19] Thus, the herein described cellulose derivatives **5**-**7** were dissolved in [EMIM][Ac] and the obtained solutions were studied in detail by rotational shear measurements. Therefore, [EMIM][Ac] and 5 wt% of each cellulose sample **5**-**7** were mixed in a sealed vessel and stirred at 60 °C for at least 12 h to ensure complete dissolution. Figure 5.4 shows the results of the viscosity - shear rate Á dependency for cellulose (**5**-**7**) / [EMIM][Ac] solutions at 20 °C. For a better comparison, the rheological behavior of a 5 wt% solution of microcrystalline cellulose (Avicel®) dissolved in [EMIM][Ac] was evaluated as well.

For all samples a Newtonian flow behavior was observed. Due to the derivatization with ILs and therefore ionic moieties, the viscosity of **5**, **6**, and **7** could be dramatically reduced compared to Avicel®. A viscosity decrease of two magnitudes was obtained for sample **5**, whereas for sample **6** and **7** a decrease of at least one magnitude could be observed. Obviously, the hydrophobic and sterically demanding butyl- (**6**) and benzyl-groups (**7**) respectively, led to an increase of viscosity compared to the derivative bearing methyl-groups (**5**). Thus, it can be assumed that the viscosity of cellulose dissolved in ILs can be reduced by regioselective deri-

vatization with ionic moieties and can be further controlled by choice of the substituent of the imidazolium group. A viscosity decrease due to polymer chain degradation during the derivatization process can be excluded by means of dynamic light scattering (DLS) measurements. For all samples, a hydrodynamic diameter in the range of 350 nm was obtained, indicating similar molecular weight values.

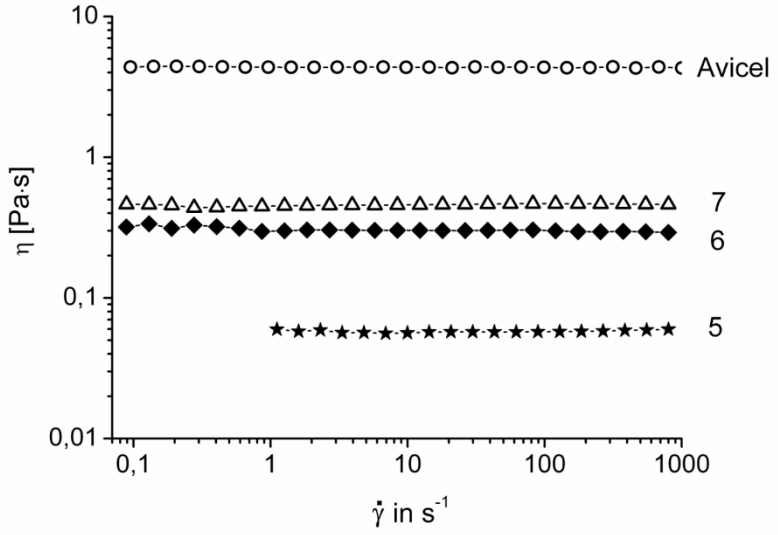


Figure 5.4 Viscosity curves of various modified (**5-7**) and unmodified (Avicel®) cellulose/[EMIM][Ac] solutions (5 wt%) in dependency of the applied shear rate Á at 20 °C.

According to literature, the temperature dependence of the viscosity, η, of many ILs is well described by the empirical Vogel-Fulcher-Tammann (VFT) equation (1),

$$\eta = \eta_0 \exp(B/(T-T_{VF})) \qquad (1)$$

where η_0, B and T_{VF} (Vogel-temperature) are adjustable parameters.[21-24] Furthermore, Budtova *et al.*[15] found out that the VFT equation also describes the temperature-viscosity dependency of cellulose/IL solutions with a very high accuracy. Therefore, the influence of the temperature on the viscosity was studied for all solutions. In Figure 5.5, the shear viscosity is plotted against temperature. As can be seen, the unmodified cellulose sample showed the highest response of viscosity decrease within temperature increase, whereas for sample **5** only

small changes of the viscosity between 20 and 60 °C were achieved. Each experimental data set was fitted by VFT (solid line) with excellent accuracies ($r^2 > 0.9999$). The calculated Vogel-temperatures were around -20 to -40 °C for **5**-**7** and 5 °C for Avicel®, respectively.

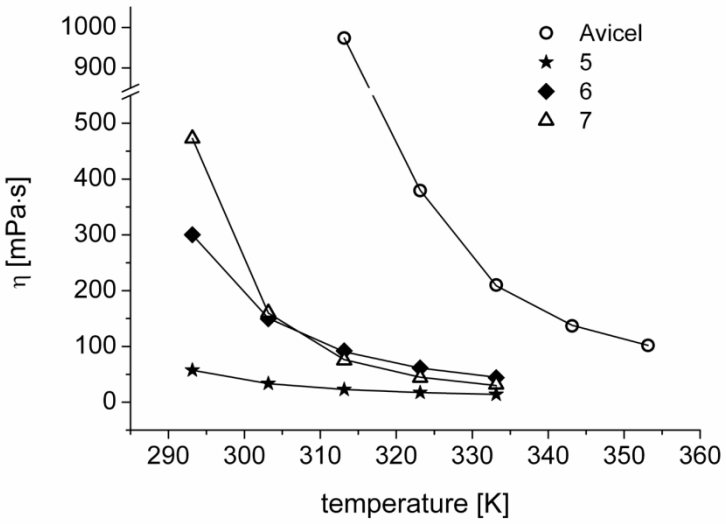


Figure 5.5 VFT plot for modified (**5**-**7**) and unmodified (Avicel®) cellulose/[EMIM][Ac]-solutions with a concentration of 5 wt% ($r^2 > 0.9999$ for all VFT fittings).

Additionally, the temperature dependence of the viscosity can also be described by the logarithmic form of the Arrhenius equation (Eq. 2),

$$\ln\eta = \ln\eta_\infty + (E_\eta / RT) \qquad (2)$$

where E_η is the flow activation energy, R is the universal gas constant and η_∞ is the viscosity at infinite temperature. The flow activation energy, E_η, is the energy barrier which must be overcome, in order for the molecules to move past each other. The value of E_η can be correlated with structural information for the solutions. In Figure 5.6, the Arrhenius plot for Avicel® and **5**-**7** is depicted. In general, it was possible to approximate each set for experimental data with a linear dependence (dashed lines) leading to accuracies of r^2 from 0.95 (Avicel®) to 0.98 (**5**-**7**).

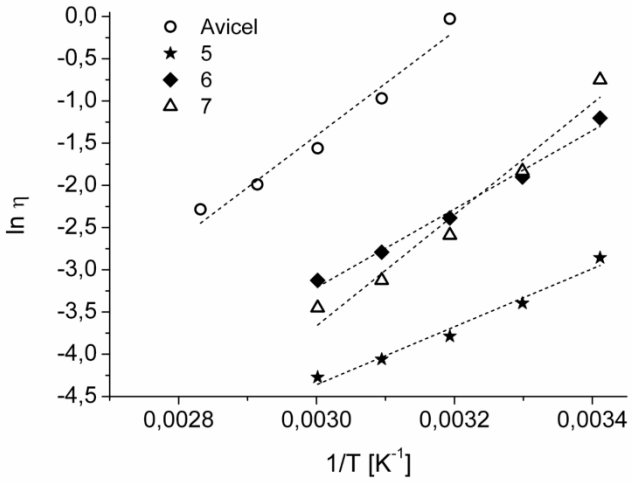


Figure 5.6 Arrhenius plot for Avicel® and **5**-**7**/[EMIM][Ac] solutions respectively at concentrations of 5 wt%. Dashed lines correspond to the Arrhenius approximation.

Therefore, E_η was deduced from the slope of the linear fit for all cellulose samples. The results for the flow activation energies and further the parameters and the uncertainties which were obtained from the VFT fitting were summarized in Table 5.2. Just like the viscosity, the values of the flow activation energy were associated to the ionic groups and the substituents of the imidazolium cation.

Table 5.2 Parameters and flow activation energies obtained from the VFT fitting and Arrhenius plot, respectively.

	wt%	**η_0 [Pa·s]**	**B [K]**	**T_{VF} [K]**	**E_η [kJ/mol]**
5	5	2.6 ± 0.2	143.9 ± 7.6	246.4 ± 1.4	29 ± 2
6	5	3.1 ± 0.7	256.8 ± 30.7	236.9 ± 3.6	39 ± 2
7	5	1.6 ± 0.4	240.3 ± 21.8	250.8 ± 1.9	55 ± 6
Avicel® (DP 260)	5	14.1 ± 0.6	148.1 ± 3.6	278. 2 ± 0.4	51 ± 6

The calculated E_η value of around 51 kJ mol^{-1} for microcrystalline cellulose (Avicel®) was in a good agreement with those reported in literature.[15] The E_η values for **5** and **6** were significantly smaller, which can be explained by the increase of the salt content in the solution due to the ionic moieties. Since a butyl-group is more sterically demanding than a methyl-group, the flow activation energy of **6** was about 10 kJ mol^{-1} larger than that of **5**. The E_η values of **7** and Avicel®/[EMIM][Ac] solutions were in the same magnitude. It can be assumed that the influence of π-π interactions between the benzyl groups overweight the benefit of the ionic moieties and therefore led to a significant increase of E_η compared to **5** and **6**.

5.3 Conclusion

The synthesis of novel polyelectrolytes based on cellulose and ionic liquids via of click chemistry was described. The structural features could be characterized by means of FTIR and NMR spectroscopy. The DS values were calculated by elemental analysis and were around 1. Furthermore, the rheological behavior of the obtained cellulose derivatives dissolved in [EMIM][Ac] was analyzed. A Newtonian flow behavior was observed for all solutions. Due to the modification, the viscosity was reduced by at least one decade compared to unmodified cellulose and could be further controlled by introducing hydrophobic and sterically demanding moieties to the imidazolium cation. The viscosity-temperature dependency could be excellently described with the Vogel-Fulcher-Tammann equation, and the flow activation energies were determined by Arrhenius plots

5.4 Experimental Details

5.4.1 Materials

1-Ethyl-3-methyl imidazolium acetate [EMIM][Ac] was obtained from BASF SE, Ludwigshafen, Germany. The amount of water and free acid was determined as 4100 ppm by coulometric Karl Fischer titration using Hydranal Coulomat AG from Fluka as anolyte.

Cellulose (Avicel® PH-101, degree of polymerization, DP 260) was obtained from Fluka. Prior to use, Avicel® was dried in a CEM Sam 255 microwave drying system and stored in a desiccator under vacuum over sicapent.

p-Toluenesulfonyl chloride (≥ 97%), and copper(II)-sulfate pentahydrate (> 99 %) were also obtained from Fluka. 1-Butylimidazole (98 %) was purchased from Aldrich and 1-methylimidazole (99 %) was obtained from Alfa Aesar. Propargyl bromide (80 wt%-solution in toluene) and 1-benzylimidazole (99 %) were purchased from Acros Organics. Sodium azide (99.5 %) was obtained from Honeywell Riedel de Haën® and sodium L(+)-ascorbate (99 %) was obtained from AppliChem (Germany).

Dialysis membranes with a molecular weight cut off (MWCO) of 3.5 kDa were obtained from Spectra/Por, Germany.

Dimethylsulfoxide-d_6 99.8 atom % D was purchased from Eurisotop® (France). Unless specified, all commercially available reagents and solvents were used without further purification.

5.4.2 Measurements and Methods

Karl Fischer titration was carried out on an 831 KF Coulometer from Metrohm, Deutsche METROHM GmbH & Co. KG, Germany.

The structures of the synthesized monomers and polymers were proven by ^{1}H- and ^{13}C-NMR spectroscopy using a Bruker Avance 400 spectrometer (^{1}H: 400.17 MHz, ^{13}C: 100.62 MHz) and a Bruker Avance DRX500 spectrometer (^{1}H: 500.13 MHz, ^{13}C: 125.77 MHz), respectively. Using DMSO-d_6 as solvent, chemical shifts were referenced to the solvent value at δ_H = 2.51 ppm and δ_C = 39.52 ppm, respectively. NMR spectra of cellulose derivatives were recorded at 60 °C, with at least 12 000 scans for ^{13}C-NMR.

The rheological behavior was studied using a Thermo Scientific HAAKE Mars II rheometer equipped with plate-plate geometry (plate diameter = 35 mm) and a temperature control system DC30/K10 from Thermo scientific to assure constant temperatures with deviations of ± 0.1 °C. All measurements were carried out with a gap width of 1 mm. Steady shear measurements were performed for all solutions at temperatures between 20 and 60 °C for cellulose derivates as well as between 40 and 80 °C for Avicel®. To avoid errors due to the shear history of the samples, preconditioning at a constant shear rate of 500 s^{-1} for 60 s was undertake, before flow and viscosity curves were recorded between 0.002 and 800 s^{-1}. All experiments were conducted from high shear rates to low shear rates.

C, H, N - elemental composition analysis was determined using a Perkin Elmer 2400 CHN analyzer.

Infrared spectra were recorded on a Nicolet 6700 FT-IR spectrometer, equipped with a diamond single bounce ATR accessory at room temperature.

Dynamic Light Scattering (DLS) experiments were carried out with a Malvern Nano ZS ZEN 3600 at 25 °C. The particle size distribution was derived from a deconvolution of the measured intensity autocorrelation function of the sample by the NNLS general purpose mode.

5.4.3 Synthesis of 6-azido-6-deoxy cellulose, 1

6-azido-6-deoxy cellulose (**1**) was synthesized from p-toluenesulfonic acid ester of cellulose (tosyl cellulose) with a degree of substitution (DS) of 1.04 and sodium azide in DMF according to ref.[3]

DS 1.015 (calculated from N-content determined by elemental analysis)

C, H, N found (%): C: 37.94 H: 5.00 N: 22.76.

IR (cm^{-1}) 3 437 (OH); 2 953 (C–H); 2 103 (N3); 1 735 (C–O); 1 036 (C–O–C)

^{1}H NMR δ/ppm (500 MHz, DMSO-d_6) = 5.41–3.09 (AGU).

^{13}C NMR δ/ppm (125 MHz, DMSO-d_6) = 102.57 (C-1, AGU); 60.44–79.62 (C-2–C-5, AGU); 51.37 (C-6, AGU)

5.4.4 Synthesis of 1-alkyl/benzyl-3-propargyl imidazolium bromides

1-Methyl-3-propargyl imidazolium bromide, 2

Propargyl bromide (2.99 g, 20.09 mmol, 80 wt% solution in toluene) was added drop wise to *N*-methylimidazole (1.5 g, 18.27 mmol) under nitrogen atmosphere at room temperature and stirred until a significant increase of the viscosity occurred. The solution was subsequently diluted with 25 ml of acetone and stirred over night. The obtained white solid was collected by filtration, washed three times with 25 ml acetone and dried under vacuum.

Yield 66 % (2.44 g, 12.14 mmol)

mp. 68.5 °C

IR (cm^{-1}) 3207, 3078 (ν CH, imidazole); 2933, 2908, 2843 (ν CH_3, CH_2); 2152 (ν C≡C); 1569, 1556 (ν C=C_{arom}); 1435, 1371 (δ CH_3, CH_2); 1157 (HCC, HCN bending, imidazole); 746 (CH bending out of plane, imidazole)

^{1}H NMR δ/ppm (500 MHz, DMSO-d_6) = 9.31 (s, 1H, -N(1)C**H**N(3)-); 7.83 (s, 1H, N(1)CHC**H-**); 7.79 (s, 1H, -N(1)C**H**CH-); 5.25 (s, 2H, -C**H_2**N(3)-); 3.90 (s, 3H, -N(1)C**H_3**); 3.87 (s, 1H, **H**C≡C-)

^{13}C NMR δ/ppm (125 MHz, DMSO-d_6) = 136.96 (N(1)**C**HN(3)); 124.41 (N(1)CH**C**H-); 122.51 (N(1)**C**HCH-); 79.33 (-C≡**C**H); 76.53 (-**C**≡CH); 38.88 (-N(3)-**C**H_2-C≡CH); 36.37 (-**C**H_3)

C, H, N $C_7H_9BrN_2$ (201.06):

calc. (%):	C: 41.82	H: 4.51	N: 13.93;
found (%):	C: 41.07	H : 4.67	N: 13.49

1-Butyl-3-propargyl imidazolium bromide, 3

Propargyl bromide (6.05 g, 40.66 mmol, 80 wt% solution in toluene) was added drop wise to *N*-butylimidazole (5 g, 40.26 mmol) under nitrogen atmosphere at room temperature and stirred until a significant increase of the viscosity was observed. The solution was subsequently diluted with 10 ml of acetone and stirred at 50 °C for 24 h. After the solvent was decanted, the raw product was washed with 100 ml toluene and dried under vacuum at 60 °C. The product obtained was amber colored and liquid at room temperature.

Yield 84 % (8.21 g, 33.77 mmol)

IR (cm^{-1}) 3135, 3070 (ν CH, imidazole); 2959, 2933, 2873 (ν CH_3, CH_2); 2124 (ν C≡C); 1559 (ν C=C_{arom}); 1462, 1337 (δ CH_3, CH_2); 1156 (HCC, HCN bending, imidazole); 750 (CH bending out of plane, imidazole)

^{1}H NMR δ/ppm (500 MHz, DMSO-d_6) = 9.51 (s, 1H, -N(1)C**H**N(3)-); 7.96 (s, 1H, N(1)CHC**H-**); 7.89 (s, 1H, -N(1)C**H**CH-); 5.30 (d, $^4J_{H,H}$= 2.52 Hz, 2H, HC≡C-C**H_2**-N(3)-); 4.26 (t, $^3J_{H,H}$= 7.26 Hz, 2H, -N(1)C**H_2**); 3.88 (t, $^4J_{H,H}$= 2.52 Hz, 1H, **H**C≡C-); 1.77 (m, 2H, -N(1)CH_2C**H_2**); 1.25 (m, 2H, -C**H_2**CH_3); 0.87 (t,$^3J_{H,H}$= 7.26 Hz, 3H, -CH_2C**H_3**)

^{13}C NMR δ/ppm (125 MHz, DMSO-d_6) = 136.43 (N(1)**C**HN(3)); 123.19 (N(1)CH**C**H-); 122.66 (-N(1)**C**HCH-); 79.37 (-C≡**C**H); 76.43 (-**C**≡CH); 49.07 (-N(1)**C**H_2-); 38.97 (-N(3)-**C**H_2-C≡CH); 31.72 (-N(1)CH_2**C**H_2-); 19.11 (-**C**H_2-CH_3); 13.65 (-CH_2-**C**H_3)

C, H, N $C_{10}H_{15}BrN_2$ (243.14)

calc. (%): C 49.40, H 6.22, N 11.52

found (%): C 49.16, H 6.66, N 11.47

1-Benzyl-3-propargyl imidazolium bromide, 4

Propargyl bromide (6.05 g, 40.66 mmol, 80 wt% solution in toluene) was added drop wise to a solution of *N*-benylimidazole (5 g, 40.26 mmol) and acetone (10 ml) under nitrogen atmosphere and stirred at room temperature for 24 h. After the solvent was decanted, the raw product was washed with 100 ml of ethyl acetate and toluene and dried under vacuum at 60 °C yielding a slightly yellow liquid.

Yield 86 % (7.54 g, 27.20 mmol)

IR (cm^{-1}) 3131, 3064 (ν CH, imidazole); 2125 (ν C≡C); 1557, 1497, 1455 (ν C=C_{arom}); 1148 (HCC, HCN bending, imidazole); 739 (CH bending out of plane, imidazole)

^{1}H NMR δ/ppm (500 MHz, DMSO-d_6) = 9.63 (s, 1H, -N(1)C**H**N(3)-); 7.97 (s, 1H, N(1)CHC**H**-); 7.89 (s, 1H, -N(1)C**H**CH-); 7.51-7.48 (m, 2H, phenyl), 7.42-7.38 (m, 3H, phenyl); 5.56 (s, 2H, -N(1)-C**H_2**-phenyl); 5.30 (d, $^{4}J_{H,H}$= 2.52 Hz, 2H, HC≡C-C**H_2**-N(3)-); 3.90 (t, $^{4}J_{H,H}$= 2.52 Hz, 1H, **H**C≡C-)

^{13}C NMR δ/ppm (125 MHz, DMSO-d_6) = 136.11 (-N(1)**C**HN(3)-); 134.79, 128.96, 128.77, 128.47 (phenyl ring); 122.83 (-N(1)CH**C**H-); 122.65 (-N(1)**C**HCH-); 79.14 (-C≡**C**H); 75.98 (-**C**≡CH); 51.88 (-N(1)**C**H_2-phenyl); 38.78 (-N(3)-**C**H_2-C≡CH)

C, H, N $C_{13}H_{13}BrN_2$ (277.16)

calc. (%):	C: 56.34	H: 4.73	N: 10.11
found (%):	C: 55.79	H: 4.79	N: 10.01

5.4.5 Synthesis of the polyelectrolytes via click chemistry

Cellulose derivative 5

6-Azido-6-deoxy cellulose (**1**) (DS 1.015, 0.3 g, 1.6 mmol) was dissolved in DMSO (30 ml) and treated with copper(II) sulfate pentahydrate (20 mg, 0.08 mmol, in 1 ml of water), sodium ascorbate (32 mg, 0.16 mmol, in 1 ml of water), and 1-methyl-3-propargyl imidazolium bromide (**2**) (0.32 g, 1.6 mmol), and stirred at 25 °C for 48 h. The crude product was isolated by precipitation in 200 ml of ethyl acetate and filtration. After purification by dialysis (water, RT, 3 d, MWCO 3.5 kDa) and freeze-drying, cellulose derivative **5** could be obtained.

DS 0.98 (calculated from N-content determined by elemental analysis)

C, H, N found (%): C: 38.81 H: 4.98 N: 18.41

^{1}H NMR δ/ppm (400 MHz, DMSO-d_6) = 9.10 (br(s), 1H, -N(1)C**H**N(3)-), 8.35 (br(s), 1H, $H_{triazole}$); 7.63 (br(s), 1H, -N(1)CHC**H**-); 7.57 (br(s), 1H, -N(1)C**H**CH-); 5.52 (br(s), 2H, imidazole-C**H_2**-triazol); 5.27-2.77 (AGU); 3.84 (br(s), 3H, C**H_3**)

^{13}C NMR δ/ppm (100 MHz, DMSO-d_6) = 140.39 (**C**-N=$N_{triazole}$); 136.86 (-N(1)**C**HN(3)-) 126.68 ($C_{triazole}$); 124.19, 122.64 (-N(1)**C**H**C**H-); 102.66 (C_1-AGU); 79.71-70.61 (C_2-C_5-AGU); 50.81 (C_6-AGU); 44.07 (imidazole-**C**H_2-triazole); 36.31 (-**C**H_3)

IR (cm^{-1}) 3390 (ν OH); 3151 (ν CH, imidazole); 3005, 2914 (ν CH_3, CH_2); 1576 (ν C=C_{arom}); 1437, 1363 (δ CH_3, CH_2); 1163 (HCC, HCN bending, imidazole); 1016 (ν C-O-C)

Cellulose derivative 6

To a solution of 6-azido-6-deoxy cellulose (**1**) (DS 1.015, 0.3 g, 1.6 mmol) in DMSO (30 ml), copper(II) sulfate pentahydrate (20 mg, 0.08 mmol, in 1 ml of water), sodium ascorbate (32 mg, 0.16 mmol, in 1 ml of water), and 1-butyl-3-propargyl imidazolium bromide (**3**) (0.39 g, 1.6 mmol) were added. The mixture was stirred at ambient temperature for 48 h and subsequently precipitated in 200 ml acetone. The polymer was collected by filtration and was further redissolved in water, dialyzed (water, 3d, RT, MWCO = 3.5 kDa), and freeze-dried.

DS 0.99 (calculated from N-content determined by elemental analysis)

C, H, N found (%): C: 43.25 H: 5.96 N: 16.52

^{1}H NMR δ/ppm (400 MHz, DMSO-d_6) = 9.45 (br(s), 1H, -N(1)C**H**N(3)-); 8.49 (br(s), 1H, $H_{triazole}$); 7.79 (br(s), 2H, -N(1)C**H**C**H**-); 5.58 (br(s), 2H, imidazole-C**H_2**-triazol); 5.51-2.75 (AGU); 4.22 (br(s), 2H, -N(1)C**H_2**-); 1.78 (br(s), 2H, -N(1)CH_2C**H_2**-); 1.26 (br(s), 2H, -C**H_2**CH_3); 0.87 (br(s), 3H, -C**H_3**)

^{13}C NMR δ/ppm (100 MHz, DMSO-d_6) = 139.75 (**C**-N=$N_{triazole}$); 136.01 (-N(1)**C**HN(3)-) 125.92 ($C_{triazole}$); 122.31 (-N(1)**C**H**C**H-); 102.13 (C_1-AGU); 79.17-70.12 (C_2-C_5-AGU); 50.11 (C_6-AGU); 48.53 (-N(1)**C**H_2-); 43.60 (imidazole-CH_2-triazole); 31.01 (-N(1)CH_2**C**H_2-); 18.47 (-**C**H_2CH_3); 12.85 (-**C**H_3)

IR (cm^{-1}) 3315 (ν OH); 3141, 3076 (ν CH, imidazole); 2959, 2932, 2872 (ν CH_3, CH_2); 1561 (ν C=C_{arom}); 1460, 1338 (δ CH_3, CH_2); 1157 (HCC, HCN bending, imidazole); 1048 (ν C-O-C); 754 (CH bending out of plane, imidazole)

Cellulose derivative 7

6-Azido-6-deoxy cellulose (**1**) (DS 1.015, 0.3 g, 1.6 mmol) dissolved in DMSO (30 ml) was converted with 1-benzyl-3-propargyl imidazolium bromide (**4**) (0.44 g, 1.6 mmol) in the presence of copper(II) sulfate pentahydrate (20 mg, 0.08 mmol, in 1 ml of water) and sodium ascorbate (32 mg, 0.16 mmol, in 1 ml of water). After stirring the mixture at ambient temperature for 48 h it was precipitated in 200 ml of acetone and the polymer was collected by filtration. Purification by dialysis (water, 3d, RT, MWCO = 3.5 kDa) and freeze-drying yielded polymer **7**.

DS 0.97 (calculated from N-content determined by elemental analysis)

C, H, N found (%): C: 46.55 H: 4.72 N: 15.51

IR (cm^{-1}) 3369 (ν OH); 3140 (ν CH, imidazole); slightly 2110 (ν N_3); 1560, 1498, 1455 (ν C=C_{arom}); 1153 (HCC, HCN bending, imidazole); 1051 (ν C-O-C)

^{1}H NMR δ/ppm (400 MHz, DMSO-d_6) = 9.62 (br(s), 1H, -N(1)C**H**N(3)-); 8.52 (br(s), 1H, $H_{triazole}$); 7.80 (br(s), 2H, - N(1)C**H**C**H**-); 7.46-7.36 (br, 5H, H_{arom}); 5.61 (br(s), 2H, imidazole-C**H_2**-triazol); 5.50 (br(s), 2H, -C**H_2**-phenyl); 5.14-2.85 (AGU)

^{13}C NMR δ/ppm (100 MHz, DMSO-d_6) = 140.48 (**C**-N=$N_{triazole}$); 136.99 (-N(1)**C**HN(3)-) 135.10 (-N(1)-**C**H_2-C_{arom}); 129.41-128.87 (C_{arom}); 126.95 ($C_{triazole}$); 123.45, 123.13 (-N(1)**C**H**C**H-); 102.65 (C_1-AGU); 78.81-69.34 (C_2-C_5-AGU); 52.62 (**C**H_2-phenyl); 50.87 (C_6-AGU); 44.46 (imidazole-**C**H_2-triazole)

5.5 References

[1] D. Klemm, B. Heublein, H.-P. Fink, A. Bohn, *Angew. Chem.* **2005**, *117*, 3422.

[2] T. Heinze, A. Koschella, *Macromol. Symp*. **2005**, *223*, 13.

[3] V. V. Rostovstev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Ang. Chem. Int. Ed.* **2002**, *42*, 2596.

[4] C. W. Tornøe, C. Christensen, M. Meldal, *J. Org. Chem.* **2002**, *67*, 3057.

[5] T. Liebert, C. Hänsch, T. Heinze, *Macromol. Rapid Commun.* **2006**, *27*, 208.

[6] T. Hasegawa, M. Umeda, M. Numata, C. Li, A.-H. Bae, T. Fujisawa, S. Haraguchi, K. Sakuraib, S. Shinkai, *Carbohydr. Res.* **2006**, *341*, 35.

[7] J. Hafrén, W. Zou, A. Córdova, *Macromol. Rapid Commun.* **2006**, *27*, 1362.

[8] T. Heinze, M. Schöbitz, M. Pohl, F. Meister, *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3853.

[9] A. Koschella, M. Richter, T. Heinze, *Carbohydr. Res.* **2010**, *345*, 1028.

[10] Y. Gao, Z. Zhang,L. Chen, W. Gu, Y. Li, *Biomacromolecules* **2009**, *10*, 2175.

[11] I. Filpponen, D. S. Argyropoulos, *Biomacromolecules* **2010**, *11*, 1060.

[12] J. Zhang, X.-D. Xu, D.-Q. Wu, X.-Z. Zhang, R.-X. Zhuo, *Carbohydr. Polym.* **2009**, *77*, 583.

[13] V. Crescenzi, L. Cornelio, C. Di Meo, S. Nardecchia, R. Lamanna, *Biomacromolecules* **2007**, *8*, 1844.

[14] B. Kosan, C. Michels, F. Meister, *Cellulose* **2008**, *15*, 59.

[15] M. Gericke, K. Schlufter, T. Liebert, T. Heinze, T. Budtova, *Biomacromolecules* **2009**, *10*, 1188.

[16] Q. L. Kuang, J. C. Zhao, Y. H. Niu, J. Zhang, Z. G. Wang, *J. Phys. Chem. B* **2008**, *112*, 10234.

[17] L.-Y. Liu, H.-Z. Chen, *J. Cellul. Sci. Technol*. **2006**, *14*, 8.

[28] R. J. Sammons, J. R. Collier, T. G. Rials, S. Petrovan, *J. Appl. Polym. Sci.* **2008**, *110*, 1175.

[19] J. R. Collier, J. L. Watson, B. J. Collier, S. Petrovan, *J. Appl. Polym. Sci.* **2009**, *111*, 1019.

[20] K. Rahn, M. Diamantoglou, D. Klemm, H. Berghmans, T. Heinze, *Angew. Makromol. Chem*. **1996**, *238*, 143.

[21] O. O. Okoturo, T. J. VanderNoot, *J. Electroanal. Chem.* **2004**, *568*, 167.

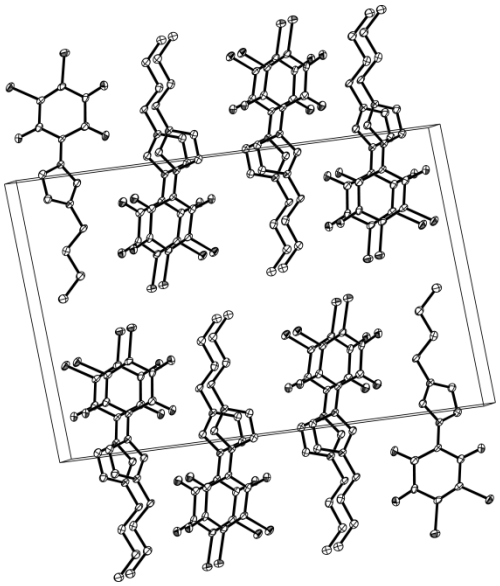
[22] R. A. Carpio, L. A. King, R. E. Lindstram, J. C. Nardi, C. L. Hussey, *J. Electrochem. Soc.* **1979**, *126*, 1644.

[23] J. R. Sanders, E. H. Ward, C. L. Hussey, *J. Electrochem. Soc.* **1986**, *133*, 325.

[24] A. P. Froba, H. Kremer, A. Leipertz, *J. Phys. Chem. B* **2008**, *112*, 12420.

Chapter 6

Novel Mesomeric Betaine Compounds with Imidazolium-enolate Structure



Abstract

The synthesis of a novel heterocyclic mesomeric betaine via quaternization reaction of 1-butylimidazole and tetrabromo-1,4-benzoquinone is presented. The structure was verified by means of X-ray single crystal analysis, NMR and IR spectroscopy. The Formation of inclusion complexes of the heterocyclic mesomeric betaine with randomly methylated (1.8) β-cyclodextrin was investigated by UV-vis spectroscopy. Furthermore, the reaction conditions were applied to poly(vinylimidazole) and 1,4-di(1*H*-imidazol-1-yl)butane to obtain functionalized polymer networks and condensate polymers, respectively.

Parts of this chapter will be published: N. Gonsior, F. Mohr, H. Ritter; submitted

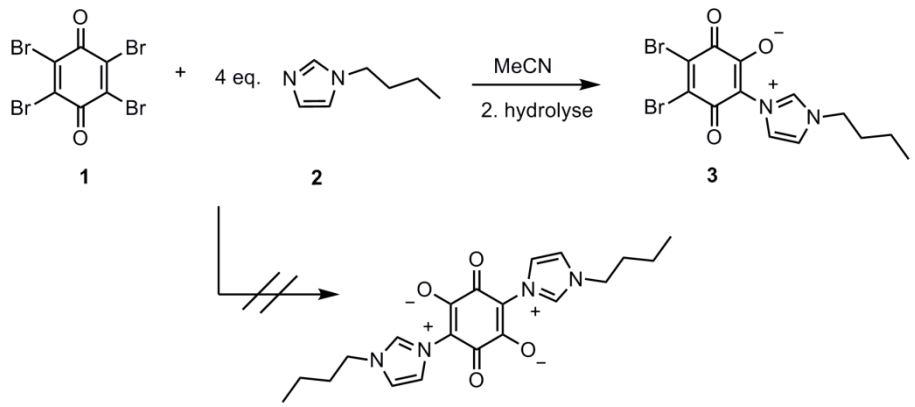
6 Mesomeric Betaines with Imidazolium-enolate Structure

6.1 Introduction

Heterocyclic mesomeric betaines [1] are interesting starting materials for heterocyclic and polymer synthesis due to there intriguing chemical properties. They have been broadly classified into four main groups, i.e. conjugated heterocyclic mesomeric betaines (CMB) which are associated with 1,3-dipoles, cross-conjugated heterocyclic mesomeric betaines (CCMB) which are associated with 1,4-dipoles, pseudo-cross-conjugated mesomeric betaines (PCCMB) which can be converted into Arduengo carbens[2,3] and N-ylides which form a subclass of CMB.[1] In the field of polymer science, CMBs such as pyridinium-olates and isoquinolinium-3-olates as well as CCMB-systems based on pyrimidinium-olates are mainly used as photosensitive materials. Different types of mesoionic monomers containing styrenic[4-6] or methacrylic[7,8] moieties have been synthesized and polymerized by Ritter *et al.*. Furthermore, also photosensitive mesoionic main-chain polymers were prepared.[9,19] Recently, A. Schmidt *et al.* described the synthesis of polymeric mesomeric betaines by quaternization of poly(4-vinylpyridine) with different halide containing quinone derivatives and subsequent hydrolysis.[11] Since the quaternization reaction is common for imidazole chemistry, e.g. the synthesis of ionic liquids, the quaternization reaction of three different imidazole compounds with tetrabromo-1,4-benzoquinone was investigated to obtain novel mesomeric betaine materials with imidazolium-enolate structure.

6.2 Results and Discussion

The quaternization (S_N2 reaction) of 1-butylimidazole (**2**) with tetrabromo-1,4-benzoquinone (p-bromanil, **1**) in acetonitrile and the subsequent quenching of the reaction mixture with water yielded dipole 2,3-dibromo-5-(1-butyl-1*H*-imidazol-3-ium-3-yl)1,4-benzochinone-6-olate (**3**) instead of the tetrapole compound (Scheme 6.1). Model compound **3** was dark red, solid, and soluble in chloroform, dichloromethane, and DMSO, but insoluble in water, acetone and toluene. The formation of **3** was confirmed by means of NMR and IR spectroscopy, as well as X-ray single crystal analysis.



Scheme 6.1 Reaction of p-bromanil (**1**) with 1-butylimidazole (**2**).

The ^{1}H-NMR spectrum of **3** is depicted in Figure 6.1. The signals for all structural features were found e.g. at 9.21 ppm, 7.81 ppm and 7.61 ppm, respectively, for the imidazolium protons, and in the range of 4.23-0.92 ppm for the butyl moiety.

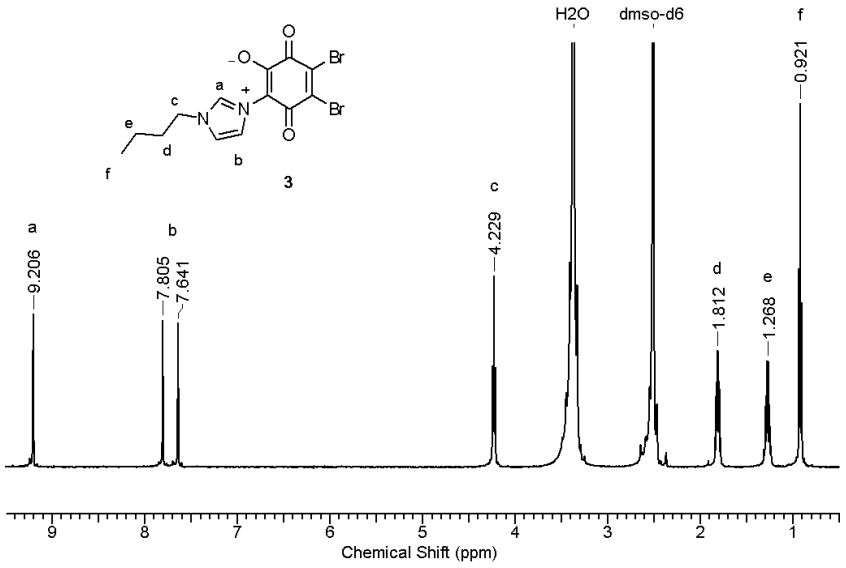


Figure 6.1 ^{1}H-NMR spectrum of mesomeric betaine **3**.

Furthermore, the ^{13}C-NMR spectrum confirms the exclusive formation of dipole **3** and the absence of the tetrapole (Figure 6.2). For the dipole formation six individual carbon signals for the benzoquinone moiety are recorded, whereas only three signals should be obtained in case of the tetrapole due to the molecule symmetry. The characteristic peaks of imidazolium

appeared at 137.3 ppm, 124.7 ppm, and 120.8 ppm, respectively. The peaks of the benzo-quinone carbons were recorded in the range of 175.4 and 111.4 ppm, whereas the signals for the butyl group appeared in the range from 48.5 to 13.3 ppm.

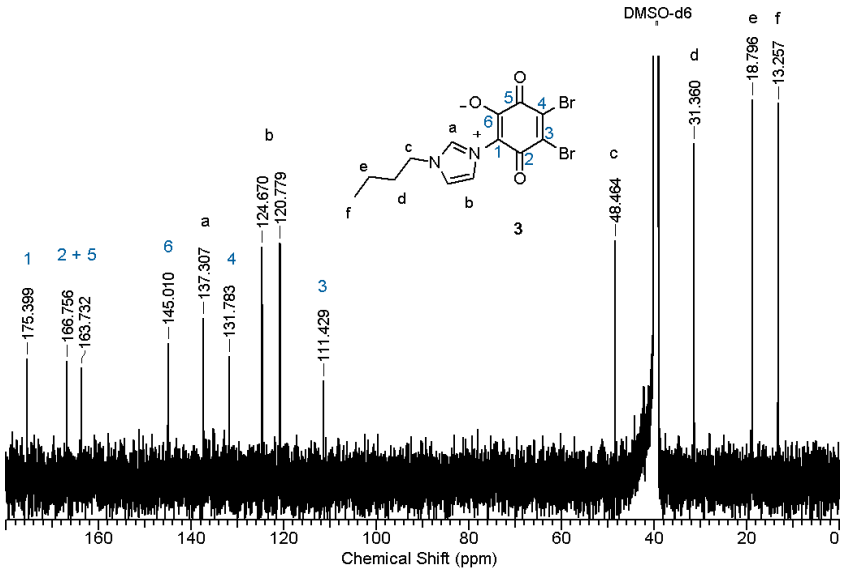


Figure 6.2 ^{13}C-NMR spectrum of dipole **3**.

Furthermore, the specific O□C□C□C□O vibration band was found at 1540 cm^{-1} in the IR spectra. By means of X-ray single crystal analysis, the structure of **3** was clearly identified (Figure 6.3, and Appendix). Single crystals were obtained by vapor diffusion method with methylene chloride and water as solvents.

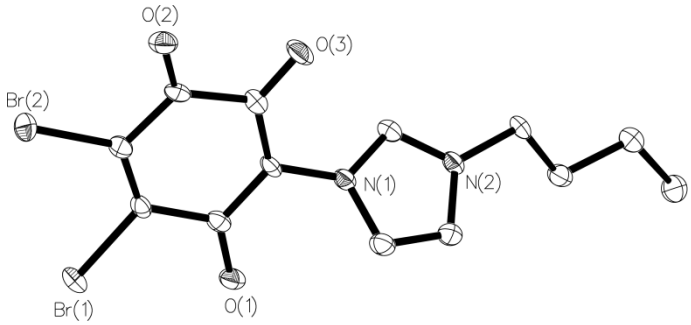


Figure 6.3 Solid state molecular structure of compound **3**. Selected bond distances [Å]: O(1)–C 1.228(4), O(2)–C 1.204(4), O(3)–C 1.241(4).

The compound crystallized in the space group $P2_{1/c}$ (No.14). The bond distances of O(3)-C and O(1)-C were 124.1(4) pm and 122.8(4) ppm, respectively. They correspond to values between C-O single and C=O double-bonds, indicating a delocalized negative charge. In the crystal packing, molecule layers were formed due to π-π-stacking of the aromatic rings (Figure 6.4).

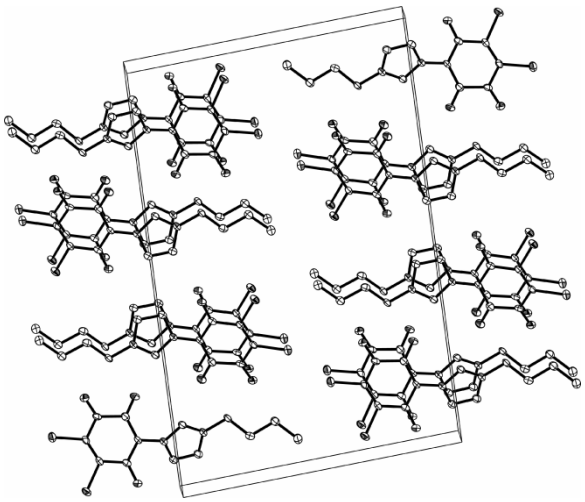


Figure 6.4 Formation of molecular layers in the crystal packing.

Regarding our interest in supramolecular chemistry and the enhancement of water solubility, the ability of **3** to form inclusion complexes with randomly methylated (1.8) β-cyclodextrin (m-β-CD) was investigated by means of UV-vis spectroscopy. Therefore, the type of inclusion complex and the complex formation constante (K) were investigated, based on the phase solubility technique. The Higuchi-Connors[12] phase diagram indicates an initial 1:1 complex, while at higher concentrations a 1:2 complex is formed (Figure 6.5, concentrations used for UV-vis measuremements see Table 6.6.4 in Appendix).

The relativley low values of the formation constant calculated for both 1:1 complex ($K_1 = 1.6 \times 10^2\ M^{-1}$) and 1:2 complex ($K_2 = 0.2 \times 10^2\ M^{-1}$) indicates only weak host/guest interactions and therefore only a slight increase of solubility in water was achieved. However, the value of K_1 is in a good agreement with those already reported for 1-butylimidazole ($1.54 \times 10^2\ M^{-1}$).[13] Thus, it can be assumed that the inclusion formation follows the suggested mechanism depicted in Scheme 6.2.

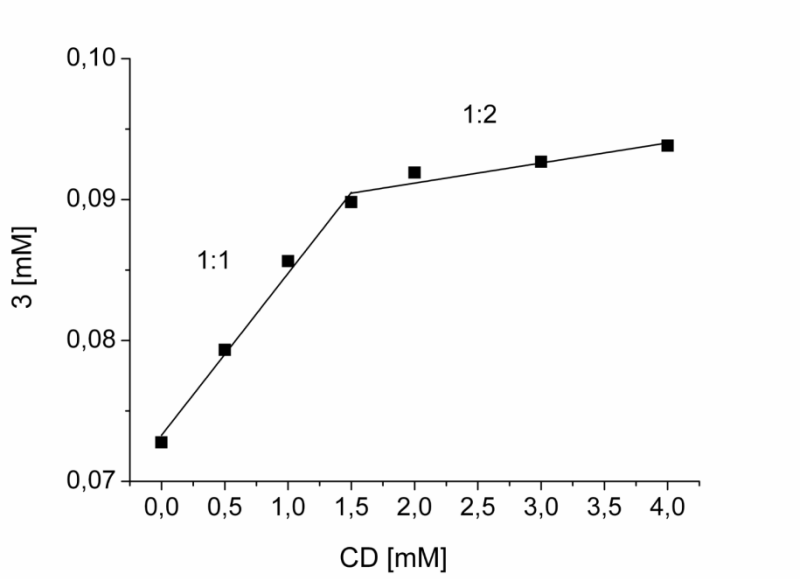
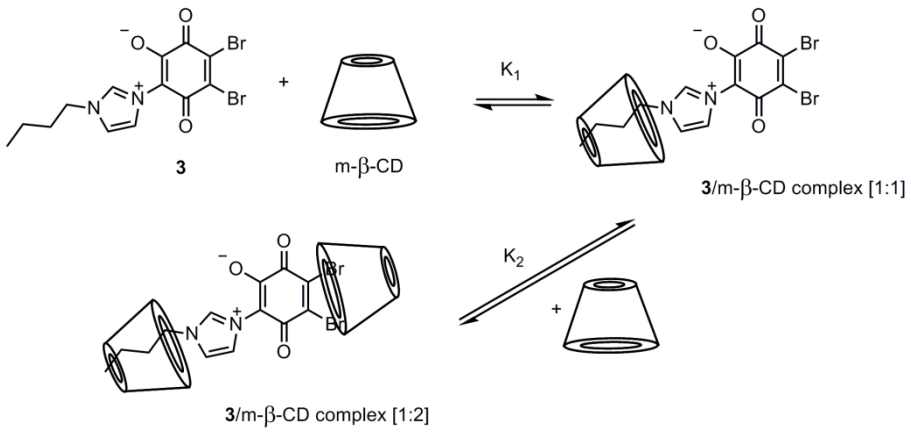


Figure 6.5 Higuchi-Connors phase diagram of **3**/m-β-CD complex.



Scheme 6.2 Mechanism of molecular association of the complex

Based on the comprehensive classification system for heterocyclic mesomeric betaines proposed by Ollis, Stanforth, and Ramsden in 1985,[1] mesoion **3** belongs to the class of conjugated heterocyclic mesomeric betaines (CMB). According to the valence bond (VB) approach for the classification, it was found that the positive and negative charges are in mutual conjugation and both are associated with the common conjugated π-electron system of the molecule. [1] An alternitive method to classify this type of conjugation, is the recognition of characteristic 1,3-dipole increments from canonical formulae. Figure 6.6 summerizes both types of classification for the CMB compound **3.**

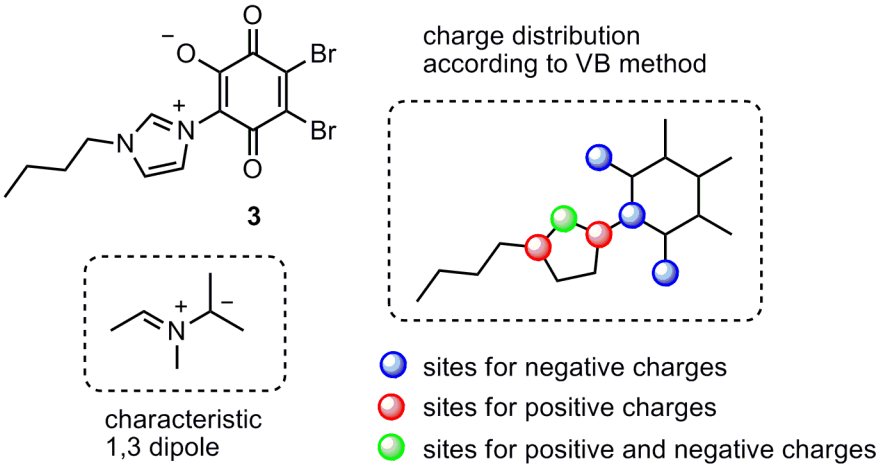
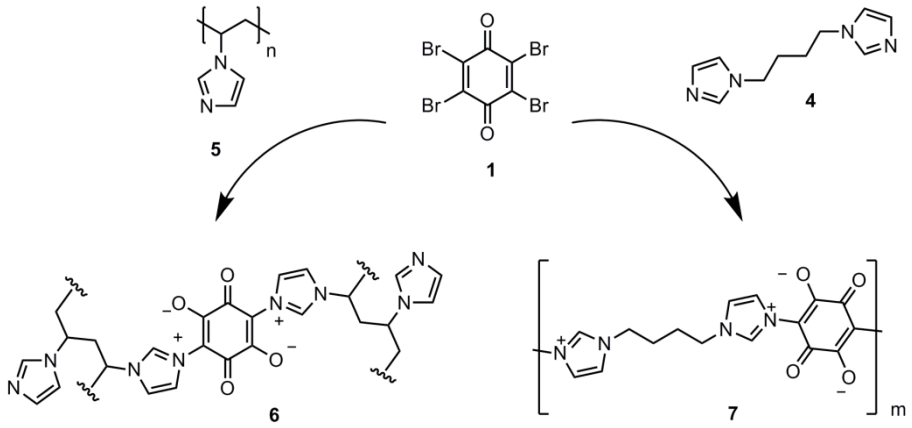


Figure 6.6 Classification of betaine **3**

According to our interest, mesoion **3** was synthesized as a model compound for further application in the field of polymer chemistry (Scheme 6.3). Therefore, p-bromanil (**1**) was reacted with different proportions of poly(vinylimidazole) (**5**) (a = 1:4, b = 1:20, c = 1:40) to obtain polymer networks, which can be represented by idealized structure **6.** Each polymer network **6 a-c** was insoluble in organic solvents. The nitrogen contents determined by elemental analysis showed, with increasing amount of **5** also the nitrogen amount increased [**6a** N: 18.49; **6b** N: 21.99; **6c** N: 23.83]. Furthermore, the intensity of the specific O□C□C□C□O vibration band at 1539 cm^{-1} was decreasing in the order of **6a** > **6 b** > **6 c**, which corresponds to a looser network structure for **6c** compared to **6a**. However, it is not possible to distinguish between inter- or intramolecular cross-linkings. To obtain condensate polymer **7, 1** was reacted with 1,4-di(1*H*-imidazol-1-yl)butane (**4**)**.** However, reaction with both monomer balance (**a**) and imbalance (**b**) led to oligomeric compounds (**7a,b**), which were soluble in water and DMSO but insoluble in e.g. $CHCl_3$, acetone or toluene. MALDI-TOF mass spectroscopy reveals a maximum repeat unit of m = 3 with 1,4-di(1*H*-imidazol-1-yl)butane end-groups on both side of the chain. The specific O□C□C□C□O vibration band was found at 1541 cm^{-1} in the IR spectra.



Scheme 6.3 Synthesis of polymer **6** and oligomer **7** based on imidazolium-enolate structures.

Thermogravimetric analyses are depicted in Figure 6.7. The weight losses of up to 10 % at temperatures lower than 120 °C are due to the extrusion of water. At higher temperatures unidentified decomposition was obtained, since the extrusion of one component results in the destruction of the polymer backbone. However, further conclusions can be made for the thermal stability. The polymers **6a-c** are stable up to 300 °C, while oligomers **7a** and **7b** decompose already at temperatures between 200 and 220 °C. Furthermore, in consideration of the temperatures present at 50 % weight loss the thermal stability decreases in order of **6c** (352 °C) > **6b** (343 °C) > **7b** (340 °C) > **6a** (334 °C) > **7a** (320 °C).

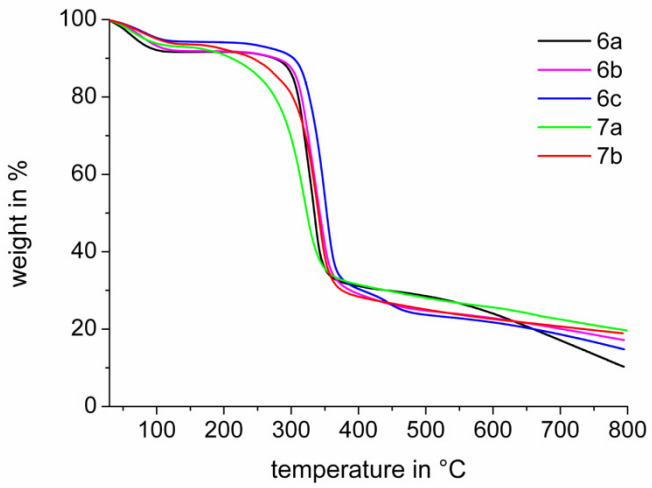


Figure 6.7 Thermogravimetric analyses of polymer network **6 a, b, c** and oligomer **7 a, b**.

6.3 Conclusion

The synthesis of novel heterocyclic mesomeric betaine **3** via quaternization reaction of 1-butylimidazole and tetrabromo-1,4-benzoquinone was presented. The structure was verified via X-ray single crystal analysis, as well as NMR and IR spectroscopy. Furthermore, mesoion **3** was classified by the comprehensive classification system for heterocyclic mesomeric betaines, as a conjugated mesomeric betaine. Inclusion complexes of **3** with m-β-CD were investigated by UV-vis spectroscopy. The Higuchi-Connors phase diagram indicated the formation of weak 1:1 and 1:2 complexes. In addition, the reaction conditions were applied to poly(vinylimidazole) and 1,4-di(1*H*-imidazol-1-yl)butane to obtain functionalized polymer networks and oligomers, which were stable at temperatures up to 300 °C and 200 °C, respectively.

6.4 Experimental Details

6.4.1 Materials

Randomly methylated (1.8) β-cyclodextrin (m-β-CD) was obtained from Wacker-Chemie GmbH (Burghausen, Germany). Prior to use, m-β-CD was dried in a CEM Sam 255 microwave drying system and stored in a desiccator under vacuum over sicapent.

1-Butylimidazole (98 %), 1,4-dichlorobutane (97 %), and azobisisobutyronitrile (98 %) were obtained from Aldrich Chemicals (Germany). 1-Vinylimidazole (99 %) and tetrabromo-1,4-benzoquinone (p-bromanil) were purchased from Alfa Aesar and 1-*H*-imidazole was obtained from AppliChem (Germany). Dimethylsulfoxide-d_6 99.8 atom % D was purchased from Eurisotop® (France). If not stated otherwise, all commercially available reagents and solvents were used without further purification.

6.4.2 Measurements and Methods

The structures of the synthesized compounds were evaluated by ^{1}H- and ^{13}C-NMR spectroscopy using a Bruker Avance DRX 500 spectrometer at 500.13 MHz for proton and 125.77 MHz for carbon. Using DMSO-d_6 as solvent, chemical shifts were referenced to the solvent value at $\delta_H = 2.51$ ppm and $\delta_C = 39.52$ ppm, respectively.

C, H, N - elemental analysis was determined using a Perkin Elmer 2400 CHN analyzer.

Infrared spectra were recorded on a Nicolet 6700 FT-IR spectrometer, equipped with a diamond single bounce ATR accessory at room temperature.

Thermogravimetric analyses (TGA) were carried out with a TA 600 Perkin Elmer (TGA combined with a DTA) in a temperature range between 303.15 and 1073.15 K under argon atmosphere. The heating rate was 10 K min^{-1}. All measurements were baseline corrected and analyzed by Pyris software.

Determination of the type of inclusion complex and the complexation constant were performed by UV-vis spectroscopy. The UV-vis spectra were recorded on a Nicolet UV540 spectrometer in the range from 190 to 400 nm in a glass cuvette with a layer thickness of 1cm. Furthermore, the change of absorbance at a wavelength of λ = 306 nm was determined according to cyclodextrin concentration.

Matrix-assisted laser desorption/ionization-time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on a Bruker Ultraflex TOF mass spectrometer. Ions formed with a pulsed nitrogen laser (25 Hz, 337 nm) were accelerated to 25 kV, the molecular masses being recorded in linear mode. 2,5-Dihydroxybenzoic acid (DBH) in acetonitrile/water (25 mg ml^{-1}) was used as a matrix. The samples (1 mg ml^{-1} in water) were mixed with the matrix solution at volumetric ratio of 1:2.

Molecular weights and molecular weight distributions were measured by size exclusion chromatography (SEC) using a Viscotek GPCmax VE2001 system that contained a column set with one Viscotek TSK guard column HHR-H 6.0mm (ID), 4 cm (L) and two Viscotek TSK GMHHR-M 7.8mm (ID), 30cm (L) columns at 60 °C. *N*,*N*-Dimethylformamide (DMF, 0.1 M LiCl) was used as eluent at a flow rate of 1 ml min^{-1}. A Viscotek VE 3500 RI detector and a Viscotek Viscometer model 250 were used. The system was calibrated with polystyrene standards with a molecular range from 580 Da to 1186 kDa.

6.4.3 Synthesis of 2,3-dibromo-5-(1-butyl-1*H*-imidazol-3-ium-3-yl)1,4-benzochinone-6-olate, 3

Tetrabromo-1,4-benzoquinone (p-bromanil, **1**) (0.845 g, 2 mmol) was dissolved in 45 ml of acetonitrile at 60 °C and 1-butylimidazole (**2**) (1 g, 8 mmol) was added. The mixture was heated to reflux for 3 h and was afterwards hydrolyzed with 40 ml of water. After filtration, acetonitrile was removed by evaporation and the resulting solution was cooled at 0 °C until a precipitate was formed. The crude product was collected by filtration and was washed three times with 50 ml of water. After recrystallization from acetic acid, **3** was obtained as a dark-red solid.

Yield 247 mg (0.61 mmol, 31 %)

IR (cm^{-1}) 3185, 3128, 3066 (ν CH, imidazole); 2960, 2915, 2877 (ν CH_3, CH_2); 1697 (C=O); 1569, 1552 (ν C=C_{arom}); 1540 (O□C□C□C□O); 1469, 1338 (δ CH_3, CH_2); 1149 (HCC, HCN bending, imidazole); 850; 736; 582

^{1}H NMR δ/ppm (500 MHz, DMSO-d_6) = 9.11 (s, 1H, -N(1)C**H**N(3)-); 7.82 (s, 1H, N(1)CHC**H-**); 7.64 (s, 1H, -N(1)C**H**CH-); 4.23 (t, $^3J_{H,H}$= 7.09 Hz, 2H, -N(1)C**H_2**); 1.81 (m, 2H, -N(1)CH_2C**H_2**); 1.27 (m, 2H, -C**H_2**CH_3); 0.92 (t,$^3J_{H,H}$= 7.41 Hz, 3H, -C**H_3**)

^{13}C NMR δ/ppm (125 MHz, DMSO-d_6) = 175.39 (-N(3)-**C**(CO^-)CO); 166.76, 163.73 (**C**=O); 145.01 (**C**O^-); 137.31 (-N(1)**C**HN(3)-); 131.78 (**C**-Br); 124.67 (N(1)CH**C**H-); 120.78 (-N(1)**C**HCH-); 111.43 (**C**-Br; 48.46 (-N(1)**C**H_2-); 31.36 (-N(1)CH_2**C**H_2-); 18.79 (-**C**H_2CH_3); 13.26 (-**C**H_3)

C, H, N $C_{13}H_{12}Br_2N_2O_3$ (404.05)

calc. (%):	C: 38.64	H: 2.99	N: 6.93
found (%):	C: 38.65	H: 2.86	N: 6.59

6.4.3.1 X-ray crystal structure analysis of 3

Single crystals of **3** were recrystallized from methylene chloride and water by vapor diffusion method, mounted in inert oil and transferred to the cold gas stream of the diffractometer. Diffraction data were collected at 150 K using an Oxford Diffraction Gemini E Ultra diffractometer [Cu-Kα-radiation (λ = 1.5418 Å)], equipped with an EOS CCD area detector and a four-circle kappa goniometer. Data integration, scaling and empirical absorption correction was carried out using the CrysAlis Pro program package.[14] The structure was solved using Direct Methods and refined by Full-Matrix-Least-Squares against F^2. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at idealised positions and refined using the riding model. All calculations were carried out using the program Olex2.[15] ***Brief summary of Crystal Data****:* $C_{13}H_{12}Br_2N_2O_3$, M = 404.07, Monoclinic, a = 15.0119(6) Å, b = 3.99067(18) Å, c = 22.8802(9) Å, β = 93.428(4)°, V = 1368.24(10) Å^3, space group $P2_1/c$ (no. 14), Z = 4, μ(Cu Kα) = 7.611, 4645 reflections measured, 2161 unique (R_{int} = 0.0437) which were used in all calculations. The final $wR(F_2)$ was 0.0921 (all data). All important crystallographic data, refinement details, bond lengths, and bond angles for **3** are summarized in Table 6.6.1, Table 6.6.2, and Table 6.6.3 respectively (see 6.6 appendix).

6.4.4 Synthesis of 1,4-di(1*H*-imidazol-1-yl)butane, 4

A mixture of 1*H*-imidazole (6.8 g, 0.1 mol) and NaOH (4.0 g, 0.1 mol) was stirred in DMSO (20 ml) at 60 °C for 1 h. 1,4-Dichlorobutane (6.4 g, 0.05 mol) was added and the mixture was stirred for further 2 h at 60 °C. Afterwards, the reaction mixture was poured into 200 ml of water and a white solid slowly precipitated. The product was collected by filtration, washed three times with water (20 ml) and was freeze-dried in order to remove remaining water.

Yield 6.18 g (0.032 mol, 65 %)

C, H, N $C_{10}H_{14}N_4$ (190.25)

calc. (%):	C: 63.16	H: 7.37	N: 29.47
found (%):	C: 62.64	H: 7.17	N: 28.15

IR (cm^{-1}) 3390 (OH, water); 3094 (ν CH, imidazole); 2939, 2860 (ν CH_2); 1641 (C=C, C=N); 1508, 1463 (ν $C=C_{arom}$); 1452, 1393 (δ CH_2); 1229; 1084; 774; 665

^{1}H NMR δ/ppm (500 MHz, DMSO-d_6) = 7.61 (s, 1H, -N(1)C**H**N(3)-); 7.14 (s, 1H, N(1)CHC**H**-); 6.88 (s, 1H, -N(1)C**H**CH-); 3.96 (m, 2H, -N(1)C**H_2**-), 1.62 (m, 2H, -C**H_2**-)

^{13}C NMR δ/ppm (125 MHz, DMSO-d_6) = 137.25 (-N(1)**C**HN(3)-); 128.43 (N(1)CH**C**H-) 119.27 (-N(1)**C**HCH-); 45.29 (-N(1)**C**H_2-); 27.71 (-**C**H_2-)

6.4.5 Syntheses of the polymers

Poly(vinylimidazole), 5

Vinylimidazole (10 g, 0.106 mol) was dissolved in THF (50 ml) under nitrogen atmosphere and AIBN (0.44 g, 2.7 mmol) was added as radical initiator. The reaction mixture was stirred for 16 h at 65 °C. The polymer precipitated during the reaction and the obtained white solid was collected by filtration, washed three times with THF (200 ml) and dried under vacuum.

GPC (DMF, PS-Standard); Mn = 150 000 g·mol^{-1}

^{1}H NMR δ/ppm (500 MHz, DMSO-d_6) = 7.46-7.01 (s, 1H, -N(1)C**H**N(3)-); 6.98-6.67 (br, 2H, -N(1)C**H**C**H**N(3)-); 3.28 - 2.79 (s (br), 1H, backbone C**H**), 2.28 - 1.61 (s (br), 2H, backbone C**H_2**)

Polymer 6a,b,c

p-Bromanil **1** (250 mg, 0.59 mmol) and poly(vinylimidazole) **5** [(**a**) = 0.22 g, (**b**) = 1.11 g, or (**c**) = 2.22 g] were suspended in acetonitrile (45 ml) and heated to reflux for 3 h. The reaction mixture was subsequently diluted with water (40 ml) for hydrolysis reaction. The crude product was collected by filtration, washed several times with water and was refluxed with ace-

tone for 1 h. After filtration and washing with acetone, polymer **6 a, b, c** was obtained as an orange or brownish solid.

C, H, N	**6a** found (%):	C: 45.02	H: 5.29	N: 18.49
	6b found (%):	C: 51.26	H: 5.35	N: 21.99
	6c found (%):	C: 54.32	H: 5.93	N: 23.83

IR (cm^{-1}) 3388 (OH, water); 3102 (ν CH, imidazole); 2939 (ν CH_2); 1632; 1538 (O□C□C□C□O); 1494, 1414 (δ CH_2); 1227; 1084; 814; 742; 662

Synthesis of Oligomer 7 with both monomer balance (7a) and monomer imbalance (7b)

p-Bromanil (**1**) (557 mg, 1.31 mmol) and 1,4-di(1*H*-imidazol-1-yl)butane (**4**) [(**a**) = 1eq and (**b**) = 2 eq, respectively) were dissolved in 45 ml of acetonitrile at 60 °C and heated to reflux for 20 h. The reaction mixture was subsequently diluted with water (40 ml) to hydrolyze the product. The solvents were evaporated and the obtained solid was redissolved in methanol. After precipitation in diethyl ether **7a** and **7b,** respectively**,** were collected by filtration and dried under vacuum to give red-colored polymers.

IR (cm^{-1}) 3380 (OH, water), 3091 (ν CH, imidazole); 2933, 2840 (ν CH_2); 1691 (C=O), 1567 (ν $C{=}C_{arom}$); 1541 (O□C□C□C□O); 1444, 1384 (δ CH_2); 1147 (HCC, HCN bending, imidazole), 842, 748.

^{1}H NMR δ/ppm (500 MHz, DMSO-d_6) = 9.27 (s, 1H, -N(1)C**H**N(3)-); 7.84 (s, 1H, N(1)CHC**H**-); 7,33 (s, 1H, -N(1)C**H**CH-); 4.28 (m, 2H, -N(1)C**H_2**-); 1.81 (m, 2H, -C**H_2**-)

6.5 References

[1] W. D. Ollis, S. P. Stanforth, C. A. Ramsden, *Tetrahedron* **1985**, *41*, 2239.

[2] A. Schmidt, A. Beutler, M. Albrecht, F. J. Ramírez, *Org. Biomol. Chem.* **2008**, *6*, 287.

[3] N. Kuhn, A. Abu-Rayyan, C. Piludu, M. Steinmann, *Heteroatom. Chem*. **2005**, *16*, 316.

[4] H. Ritter, R. Sperber, C. M. Weillhuhn, *Macromol. Chem. Phys*. **1994**, *195*, 3823.

[5] H. Ritter, R. Sperber, *Macromol. Rapid Commun.* **1995**, *16*, 407.

[6] T. Deutschmann, H. Ritter, *Macromol. Chem. Phys.* **2000**, *201*, 1200.

[7] A. Theis, H. Ritter, *Des. Monomers Polym*. **2001**, *4*, 177.

[8] A. Theis, H. Ritter, *Macromolecules* **2003**, *36*, 7552.

[9] T. Deutschmann, H. Ritter, *Macromol. Rapid Commun.* **1996**, *17*, 723.

[10] A. Theis, H. Ritter, F. Bohme, C. Klinger, B. Menges, S. Mittler, *Chem. Mat.* **2002**, *14*, 2109.

[11] A. Schmidt, M. Albrecht, *Z. Naturforsch*. **2008**, *63b*, 465.

[12] T. Higuchi, K. A. Connors, *Adv. Anal. Chem. Instrum.* **1965**, *12*, 189.

[13] M. V. Rekharsky, Y. Inoue, *Chem. Rev*. **1998**, *98*, 1875.

[14] CrysAlis Pro version 171.33.42, Oxford Diffraction Ltd. (**2009**).

[15] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339.

6.6 Appendix

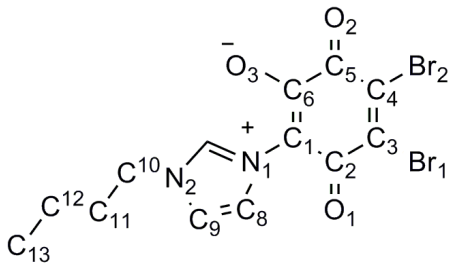


Figure 6.6.1 Numbering for the assignment of the bond lengths and angles.

Table 6.6.1 Bond lengths for **3** (The numbering corresponds to that in Figure 6.6.1)

atom	atom	length [Å]	atom	atom	length [Å]
Br1	C3	1.874(3)	C9	C8	1.345(5)
Br2	C4	1.868(3)	C4	C3	1.337(5)
O3	C6	1.241(4)	C4	C5	1.503(5)
O2	C5	1.204(4)	C2	C1	1.424(5)
N2	C9	1.379(4)	C2	C3	1.514(5)
N2	C7	1.320(4)	C12	C11	1.529(5)
N2	C10	1.493(4)	C12	C13	1.521(5)
O1	C2	1.228(4)	C1	C6	1.398(5)
N1	C7	1.349(4)	C6	C5	1.544(5)
N1	C8	1.379(5)	C10	C11	1.505(5)
N1	C1	1.431(4)			

Table 6.6.2 Bond angels for **3** (The numbering corresponds to that in Figure 6.6.1)

atom	atom	atom	angel [°]	atom	atom	atom	angel [°]
O3	C6	C1	126.3(3)	C7	N2	C9	109.1(3)
O3	C6	C5	116.8(3)	C7	N2	C10	126.1(3)
O2	C5	C4	121.6(3)	C7	N1	C8	107.9(3)
O2	C5	C6	119.9(3)	C7	N1	C1	126.4(3)
N2	C7	N1	108.4(3)	C8	N1	C1	125.7(3)
N2	C10	C11	112.6(3)	C8	C9	N2	107.0(3)
O1	C2	C1	124.7(3)	C1	C2	C3	116.5(3)
O1	C2	C3	118.8(3)	C1	C6	C5	116.8(3)
C9	N2	C10	124.6(3)	C6	C1	N1	118.4(3)
C9	C8	N1	107.5(3)	C6	C1	C2	124.6(3)
C4	C3	Br1	122.2(3)	C10	C11	C12	111.2(3)
C4	C3	C2	123.8(3)	C3	C4	Br2	124.9(3)
C4	C5	C6	118.5(3)	C3	C4	C5	119.2(3)
C2	C1	N1	117.0(3)	C5	C4	Br2	115.9(2)
C2	C3	Br1	114.0(2)	C13	C12	C11	112.5(3)

Table 6.6.3 Crystal data and structure refinement for **3**

	3
Empirical formula	$C_{13}H_{12}Br_2N_2O_3$
Colour	dark-red
M [g mol^{-1}]	404.07
Crystal system	Monoclinic
Space group	$P2_1/c$
a, b, c [Å]	15.0119 (6), 3.99067 (18), 22.8802 (9)
α, β/ γ [°]	90.00, 93.428 (4), 90.00
Volume [Å^3]	1368.24 (10)
Z	4
ρ_{calc} [mg mm^{-3}]	1.962
μ [mm^{-1}]	7.611
F (0 0 0)	792
Crystal size [mm^3]	0.1 × 0.02 × 0.02
θ range for data collection [°]	3.87 to 62.43
Reflections collected	4645
Independent reflections	2161
Parameters	182
Goodness-of-fit	1.038
R_1 [I>2σ (I)]	0.0317
wR_2 [all data]	0.0921
Largest diff. peak/hole [e Å^{-3}]	0.709/-0.878

Table 6.6.4 Concentration of mesomeric betaine compound **3** and randomly methylated (1.8) β-cyclodextrin (m-β-CD) used for UV-vis measurements.

concentration [mmol l^{-1}]		molar ratio
3	**m-β-CD**	
2	0	1:0
2	0.5	1:0.25
2	1	1:0.5
2	1.5	1:0.75
2	2	1:1
2	3	1:1.5
2	4	1:2

Publications and Conference Contributions

During the course of this thesis, the following papers and posters have been published (or submitted):

Publications

[1] M. Bardts, **N. Gonsior**, H. Ritter; "Polymer Synthesis and Modification by Use of Microwaves", *Macromol. Chem. Phys.* **2008**, *209*, 25.

[2] **N. Gonsior**, S. Schmitz, H. Ritter; "Thermal Sensitivity of tert-Butyloxycarbonylmethyl Modified Polyquats in Condensed Phase and Solubility Properties of Copolymers with N-isopropylacrylamide", *Marcomol. Chem. Phys.* **2010**, *211*, 1695.

[3] **N. Gonsior**, M. Hetzer, W.-M. Kulicke, H. Ritter; "First Studies on the Influence of methylated β-Cyclodextrin on the Rheological Behavior of 1-Ethyl-3-methyl Imidazolium Acetate", *J. Phys. Chem. B* **2010**, *114*, 12468.

[4] **N. Gonsior**, H. Ritter; "UCST-Behavior of Cyclodextrin Containing Poly(Pseudo-Betaines) Based on Supramolecular Structures", submitted.

[5] **N. Gonsior**, H. Ritter; "Rheological Behavior of Polyelectrolytes Based on Cellulose and Ionic Liquids Dissolved in 1-Ethyl-3-Methyl Imidazolium Acetate", submitted.

[6] **N. Gonsior**, F. Mohr, H. Ritter; "Synthesis of Mesomeric Betaine Compounds with Imidazolium-enolate Structure", submitted.

Poster presentations

[1] **N. Gonsior**, P. Kerep, H. Ritter; "Microwave and Selectivity in Polymerization Reaction" 5th International Microwaves in Chemistry Conference 2007, London GB

[2] **N. Gonsior**, S. Amajjahe, H. Ritter; "Polymeric Ionic Liquids: Synthesis, Polymerization, and Cyclodextrins" 2nd Congress on Ionic Liquids 2008, Yokohama Japan

[3] **N. Gonsior**, H. Ritter; "Methacrylated Cyclodextrin Salt via Click Chemistry" 3rd Congress on Ionic Liquids 2009, Cairns Australia

Die hier vorgelegte Dissertation habe ich eigenständig und ohne unerlaubte Hilfe angefertigt. Die Dissertation wurde in der vorgelegten oder in ähnlicher Form noch bei keiner anderen Institution eingereicht. Ich habe bisher keine erfolglosen Promotionsversuche unternommen.

Düsseldorf, den 30.06.2010

(Nina Gonsior)