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Cationic Polybenzoxazines. A Novel Polyelectrolyte Class with Adjustable Solubility and Unique Hydrogen-Bonding Capabilities

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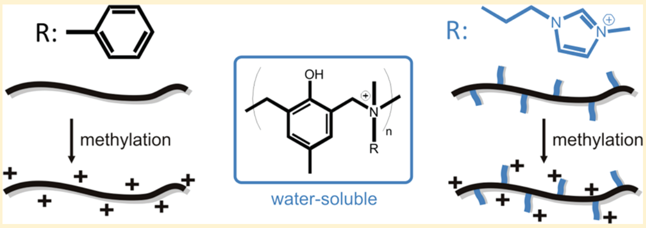

ABSTRACT: This article fuses the world of benzoxazine chemistry with the field of polyelectrolyte chemistry and introduces a new approach toward water-soluble polybenzoxazines. The synthesis of a novel class of polybenzoxazine-based polyelectrolytes carrying cationic charges in the side chain and/or the backbone is described. Tertiary nitrogen atoms of the backbone or side chain have been methylated in a polymer analogous reaction leading to cationic polybenzoxazines with structure dependent, adjustable solubility in various solvents including water providing unique hydrogen-bonding capabilities. The polymers have been investigated by ^{13}C NMR, SEC, TGA, and DSC.

1. INTRODUCTION

Polymeric compounds bearing quaternary ammonium moieties are a class of polyelectrolytes with unique properties resulting from the distribution and density of the positive charges along the macromolecule. Like other polyelectrolytes, these polymers find a wide range of different applications in daily life and industrial processes as they can function as stabilizers, flocculants, thickeners, antibacterial agents, dye transfer inhibitors, or drag reducers for example and are a valuable additive in water treatment, oil recovery, soaps, shampoos, and cosmetics.[1]

Different synthetic pathways have been described in literature as chain growth and step growth polymerization of suitable cationic monomers or species that turn cationic during the polymerization process as well as chemical transformations of uncharged reactive precursor polymers.[1]

The most significant polymer-analogous reactions to introduce quaternary nitrogen in the polymer are the quaternization of a halogen-containing polymer with a tertiary amine, the arylation or alkylation of a polymeric tertiary amine, the addition of agents like 2,3-epoxypropyltrimethylammonium chloride to polymers containing OH-groups or the base-catalyzed Mannich reaction of a polymeric amide with formaldehyde and dimethylamine followed by quaternization.[1] Depending on the location of the cationic charge, one differs between pendant (charges located in the side chain) and integral type (charges in the backbone) systems. Typical examples for the integral type are ionenes, polycations that carry quaternary nitrogen as the charged species in the polymer backbone.[2] They can be synthesized by either the Menshutkin reaction of bis-tertiary amines and dihalides,[3,4] the self-condensation of aminoalkyl halides or by the polyaddition of dimethylamine or the reaction of bis-tertiary amines[3,4] or secondary amines with epichlorohydrin in the presence of HCl.[4]

This publication introduces a new species of linear cationic water-soluble polyelectrolytes of pendant and integral type holding quaternary ammonium groups based on 1,3-benzoxazine chemistry. In contrast to a previous contribution by Yagci et al. in which the quaternization of pyridine-substituted benzoxazine monomer has been used to create intercalated benzoxazine clay,[5] our approach aims at water-solubility by creating linear polybenzoxazine polyelectrolytes derived by thermal ring-opening polymerization followed by a polymer-analogous quaternization reaction.

Benzoxazines have gained increasing interest over the past decade due to their convenient synthesis and their ability to thermally polymerize without the addition of catalysts or initiators.[6] Depending on the molecule design, highly cross-linked thermoset materials with excellent material properties can be obtained that open a wide range of possible applications from composite materials over brake adhesives to printed circuit boards.[7] By blocking the *para*-position of the phenolic ring, network formation can be prevented and linear polybenzoxazines[8,9] can be obtained offering new options for this vivid field of research (Scheme 1).

Recently our group investigated water-soluble benzoxazine systems that are able of stabilizing oil-in-water (o/w) emulsions. The first publication in this regard introduced nonionic surfactants containing thermally polymerizable benzoxazine units.[10] Another article picked up this idea and combined it with the concept of advanced chemical induced phase separation (advanced CIPS) to obtain main-chain type benzoxazine prepolymers that function as protective colloids in emulsion systems and are furthermore able to improve fracture toughness of a rigid matrix.[11,12]

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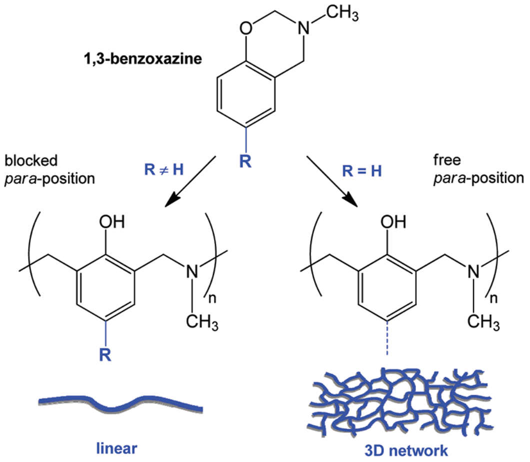
Scheme 1. Principle of the Polymerization of Benzoxazines Leading to Linear or Cross-Linked Polybenzoxazines Using the Example of *N*-methyl-3,4-dihydro-2*H*-1,3-benzoxazine (P-m) Derivates



Following the pathway of transferring benzoxazines to aqueous media, this article fuses the world of benzoxazine chemistry with the field of polyelectrolyte chemistry and introduces a new approach toward water-soluble polybenzoxazines.

2. EXPERIMENTAL SECTION

2.1. Materials. Paraformaldehyde, bisphenol A, *N*-(3-aminopropyl)-imidazole and *p*-cresol were purchased from Acros Organics, aniline was purchased from Merck, and dimethyl sulfate was purchased from Fluka. All chemicals were used as received.

2.2. Synthesis. *3,4-Dihydro-6-methyl-3-phenyl-2H-1,3-benzoxazine (pC-a).* pC-a was synthesized from *para*-cresol, aniline, and paraformaldehyde. The reactants were mixed in a 1:1:2.2 molar ratio of *p*-cresol, aniline, and paraformaldehyde resulting in a 10% excess of paraformaldehyde. The reaction was carried out in toluene with a 50 wt % solid content and refluxed for 5 h. Upon completion of the 5 h, the product was allowed to cool, and it was washed three times with a 1.0 M NaOH solution followed by three times with deionized water. After evaporation of the solvent the product was degassed for 2 h at 80 °C to remove residual solvent. A white crystalline solid was obtained (yield: 87%).

3-[3-(1H-imidazole-1-yl)propyl]-6-methyl-3,4-dihydro-2H-1,3-benzoxazine (pC-napi). pC-napi was synthesized from *p*-cresol, *N*-(3-aminopropyl)imidazole, and paraformaldehyde. Synthesis was carried out in analogy to the synthesis of pC-a. A highly viscous yellow product was obtained (yield: 79%).

pC-a/pC-napi Resin Mixtures. Mixtures of different molar ratios (1:1, 3:2, 7:3, 4:1, 9:1) of pC-a to pC-napi were prepared by mixing the required amounts of the previously synthesized monomers at 80 °C.

Poly(3,4-dihydro-6-methyl-3-phenyl-2H-1,3-benzoxazine) (PpC-a). The polymer PpC-a was synthesized through the thermal curing of pC-a. The monomer pC-a was cured in an autoclave at 160 °C for 5 h under 6 bar to prevent vaporization of the pC-a. Afterward the product was postcured for 2 h at 200 °C in an oven. The resulting polymer was purified three times by dissolving it in THF and precipitation in chilled methanol. The supernatant was decanted and disposed while the precipitate was put under vacuum at room temperature for 1 day to give a red brown solid (yield: 72%).

Poly(3-[3-(1H-imidazole-1-yl)propyl]-6-methyl-3,4-dihydro-2H-1,3-benzoxazine) (PpC-napi). The polymer PpC-napi was synthesized through the thermal curing of pC-napi. The monomer pC-napi was transferred into aluminum pans for curing. Curing was done in an autoclave at 160 °C for 5 h under 6 bar. The resulting polymer was purified by dissolving it in ethanol and precipitating it three times in chilled methanol. The supernatant was decanted and discarded, while the precipitate was put under vacuum at room temperature for 1 day to give a yellow solid (yield: 74%).

Poly[(3,4-dihydro-6-methyl-3-phenyl-2H-1,3-benzoxazine)-co-(3-[3-(1H-imidazole-1-yl)propyl]-6-methyl-3,4-dihydro-2H-1,3-benzoxazine)] (PpC-a/napi). The copolymer PpC-a/napi was synthesized through the thermal curing of pC-a/pC-napi resin mixture in an autoclave at 160 °C for 5 h under 6 bar of pressure. The resulting polymer was purified by dissolving it in THF and precipitating it three times in chilled methanol. The supernatant was decanted and disposed, while the precipitate was put under vacuum at room temperature for 1 day to give a yellow solid (yield: 75%).

Methylated Poly(3,4-dihydro-6-methyl-3-phenyl-2H-1,3-benzoxazine) (MePpC-a). PpC-a was dissolved in DMSO and reacted with 2 mol of dimethyl sulfate for every 1 mol of monomer units. The solution was heated to 80 °C, and dimethyl sulfate was added dropwise. The solution was stirred at 80 °C for 4 h. The solvent was evaporated to give a red brown solid. The crude product was dissolved in methanol and precipitated three times in diethyl ether. After precipitation, the supernatant was decanted and the precipitate was dried under vacuum overnight to give a red brown solid (yield: 70%).

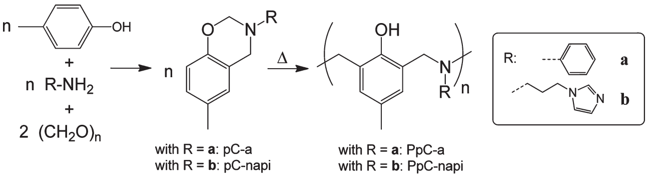
Methylated Poly(3-[3-(1H-imidazole-1-yl)propyl]-6-methyl-3,4-dihydro-2H-1,3-benzoxazine) (MePpC-napi). PpC-napi) was dissolved in ethanol and reacted with 2 mol of dimethyl sulfate for every 1 mol of monomer units. The solution was heated to reflux, and dimethyl sulfate was added dropwise. The solution was stirred under reflux for 4 h. The solvent was evaporated to give a yellow solid. The crude product was dissolved in ethanol and precipitated three times in diethyl ether. After precipitation, the supernatant was decanted and the precipitate was dried under vacuum overnight to give a yellow solid (yield: 64%).

Methylated Poly[(3,4-dihydro-6-methyl-3-phenyl-2H-1,3-benzoxazine)-co-(3-[3-(1H-imidazole-1-yl)propyl]-6-methyl-3,4-dihydro-2H-1,3-benzoxazine)] (MePpC-a/napi) (Molar Ratio 1:1, 3:2, 7:3). PpC-a/napi was dissolved in ethanol and reacted with 2 mol of dimethyl sulfate for every 1 mol of monomer units. The solution was heated to reflux, and dimethyl sulfate was added dropwise. The solution was stirred under reflux for 4 h. The solvent was evaporated to give a yellow solid. The crude product was dissolved in ethanol and precipitated three times in diethyl ether. After precipitation, the supernatant was decanted and the precipitate was dried under vacuum overnight to give a yellow solid (yield: 67%).

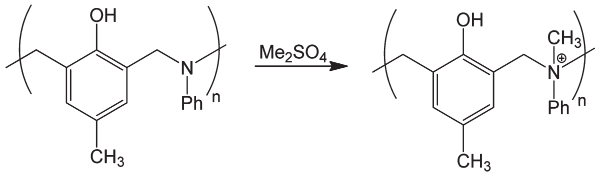
Methylated Poly[(3,4-dihydro-6-methyl-3-phenyl-2H-1,3-benzoxazine)-co-(3-[3-(1H-imidazole-1-yl)propyl]-6-methyl-3,4-dihydro-2H-1,3-benzoxazine)] (MePpC-a/napi) (Molar Ratio 4:1, 9:1). PpC-a/napi was dissolved in DMSO and reacted with 2 mol of dimethyl sulfate for every 1 mol of monomer units. The solution was heated to 80 °C, and dimethyl sulfate was added dropwise. The solution was stirred at 80 °C for 4 h. The solvent was evaporated to give a red brown solid. The crude product was dissolved in methanol and precipitated three times in diethyl ether. After precipitation, the supernatant was decanted and the precipitate was dried under vacuum overnight to give an orange solid (yield: 67%).

6,6′-(Propane-2,2-diyl)bis(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazine) (B-a). To 10 mL of toluene, paraformaldehyde (44 mmol, 1321.32 mg, 10% excess), bisphenol A (20 mmol, 2282.90 mg), and aniline (20 mmol, 1862.60 mg) were added and refluxed for 5 h under stirring. The reaction mixture was washed three times with 1 N NaOH aqueous solution and three times with deionized water. After removal of

Scheme 2. Synthesis of 3,4-Dihydro-6-methyl-3-phenyl-2*H*-1,3-benzoxazine (pC-a) and 3-[3-(1*H*-Imidazole-1-yl)propyl]-6-methyl-3,4-dihydro-2*H*-1,3-benzoxazine (pC-napi) and Their Polymerization to Linear Polybenzoxazines



Scheme 3. Schematic Illustration of the Synthesis of Polyelectrolyte *Me*PpC-a by Methylation of the Tertiary Nitrogen in the Backbone of the Linear Polybenzoxazine Precursor



solvent via rotary evaporator, the product was heated to 80 °C for another 2 h while high vacuum was applied to remove residual solvent. The procedure afforded a white solid (yield: 84%).

2.3. Instrumentation. Quantifiable ^{13}C NMR spectra were obtained on a Bruker 500 MHz Avance NMR spectrometer using inverse-gated decoupling. Size exclusion chromatography (SEC) was measured with Waters Alliance instrument with UV detector 2487 (254 nm) or refractive index detector 2410. THF was used as a carrier solvent at a flow rate of 0.9 mL min^{-1} at 35 °C. Three polystyrene gel columns (Waters Styragel HR1, 3 and 5) were used with measurable molecular weights from 1×10^2 to 2×10^7. Polystyrene standards were used for calibration to determine M_n and M_w/M_n. Differential scanning calorimetry (DSC) was measured on a TA Instruments Q1000 analyzer. Samples (6−7 mg) were heated from −50 to 250 °C at a heating rate of 5 °C/min under nitrogen. Thermogravimetric analysis (TGA) was carried out on a TA Instruments Q5000 analyzer. Samples (6−7 mg) were heated from room temperature to 500 °C at a heating rate of 5 °C·min^{-1} under nitrogen.

3. RESULTS AND DISCUSSION

Linear cationic polyelectrolytes of pendant and integral type holding quaternary ammonium groups based on 1,3-benzoxazine chemistry have been successfully synthesized. Two different monomers based on *p*-cresol have been created according to Scheme 2. The methyl group of *p*-cresol serves as a blocking group to inhibit *para*-substitution and guide the thermal ring-opening polymerization process to linear polybenzoxazines (Scheme 2).

These linear polybenzoxazines served as precursors for the synthesis of cationic polyelectrolytes. Because of the different chemical nature of the side groups either integral type or a combination of integral and pendant type have been received. The aniline-based polybenzoxazine has been methylated at the tertiary nitrogen in the polymer backbone using dimethyl sulfate as the alkylation agent (Scheme 3). This reaction leads to cationic integral type polyelectrolytes. The imidazole-based polybenzoxazine on the other hand offers a second methylation side at the nitrogen in the imidazole ring (Scheme 4). Therefore, linear polybenzoxazine polyelectrolytes holding cationic charges in the backbone and the side chain have been obtained.

Scheme 4. Schematic Illustration of the Synthesis of Polyelectrolyte *Me*PpC-napi by Methylation of the Tertiary Nitrogen in the Backbone of the Linear Polybenzoxazine Precursor and the Nitrogen of the Imidazole Group in the Side Chain

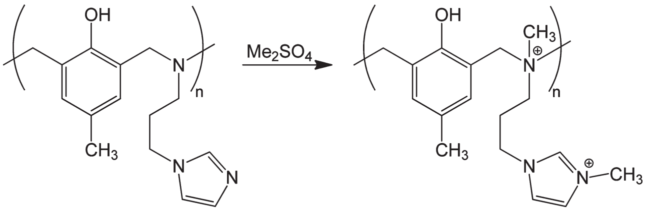


Table 1. Apparent Molecular Weights and Polydispersity Indices (PDIs) of the Linear Polybenzoxazines Determined by Size Exclusion Chromatography (SEC) (Eluent: DMSO)

	M_w (g·mol^{-1})	M_n (g·mol^{-1})	PDI (M_w/M_n)
PpC-a	6300	2400	2.6
PpC-napi	5400	2200	2.4
PpC-a/napi(1:1)	5200	2000	2.5
PpC-a/napi(1:1)[a]	10 800	3400	3.2

[a] With 2 wt % B-a.

Besides the homopolymers of PpC-a and PpC-napi, random copolymers of pC-a and pC-napi have been synthesized. The copolymer, PpC-a/napi, has been methylated according to the principles for the synthesis of the homopolymers (Scheme 3 and 4).

In general polybenzoxazines are hydrophobic materials of low water uptake.[13] This property is highly desired for most applications and a standard measure in material science. Because of the introduction of cationic charges and the transformation of polybenzoxazines in polyelectrolytes, water solubility can be achieved which is quite unusual for this class of materials. A detailed investigation can be found in chapter 3.2.

All structures were analyzed in detail. The apparent molecular weights and the according polydispersity indices have been determined by size exclusion chromatography (SEC) (Table 1). Since the molecular weights of the nonmethylated are approximately identical to the values of the methylated species, SEC experiments were carried out with the uncharged polymers to avoid strong interactions with the stationary phase of the SEC column. Weight-averaged molecular weights of 5000−6000 g·mol^{-1} have been achieved with polydispersities of around 2.5. From previous work, it is known that, in benzoxazine polymerizations, the chain growth is strongly dependent on the chemical structure and reaction conditions, e.g., the use of catalyst or varying reaction temperatures.[14,15] However, in case of monobenzoxazine polymerization usually low molecular weight species of similar or even lower M_w values are obtained.[16]

The molecular weight can be increased by addition of 2 wt % of a difunctional benzoxazine, 6,6′-(propane-2,2-diyl)bis(3-phenyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazine) (B-a), to the

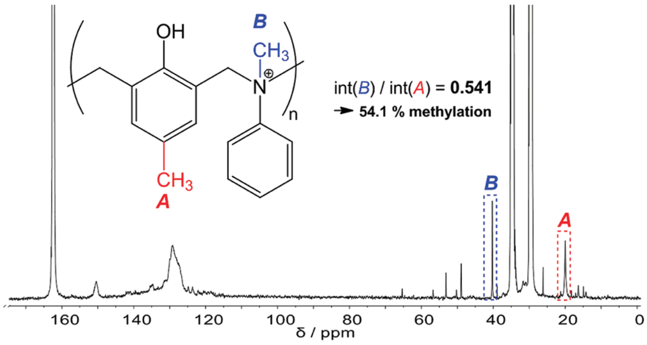


Figure 1. Quantifiable ^{13}C NMR of the methylated polybenzoxazine structure of *Me*PpC-a in DMF-d_7. The degree of methylation of the backbone nitrogen (B) was determined to be 54.1%.

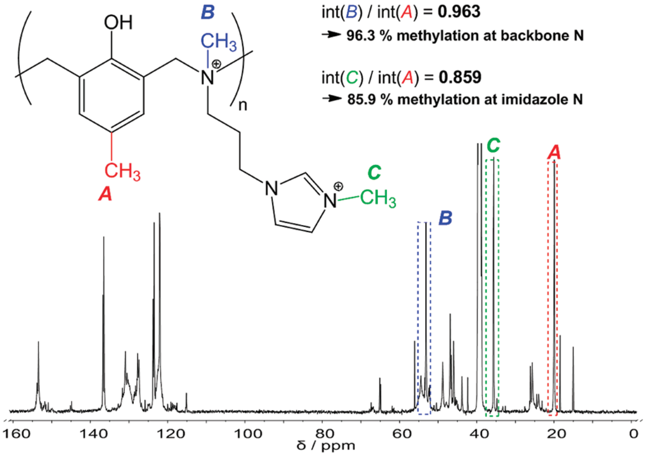


Figure 2. Quantifiable ^{13}C NMR of the methylated polybenzoxazine *Me*PcP-napi in DMSO-d_6. The degrees of methylation of the polymer backbone (B) and the imidazole in the side chain were determined to be 96.3% and 85.9%, respectively.

monomer before curing leading to molecular weights of around 11,000 g·mol^{-1}.

3.1. Characterization of Polyelectrolytes. *^{13}C NMR Analysis.* The chemical structures of the polyelectrolytes have been confirmed by quantifiable ^{13}C NMR. The spectrum of *Me*PpC-a is shown in Figure 1. The spectrum allows the calculation of the degree of methylation by comparing the integrals of the signals of the methyl group in *para*-position to the hydroxyl group at 20 ppm and the methyl group at the quaternary nitrogen at 40 ppm. An analysis via ^{1}H NMR could not be achieved due to overlapping signals. 54.1% of the tertiary nitrogen atoms in the backbone of the precursor were successfully transferred into charged quaternary species. The resulting polymer can be regarded as a copolymer of charged and uncharged repeat units. These different structures lead to slightly shifted signals that let the spectrum appear crowded. The aromatic carbons of the side group and the backbone can be found in the region of 120 to 140 ppm. The peaks overlapping at 150 ppm can be assigned to the aromatic carbons attached to the oxygen and nitrogen. The methylene groups between the nitrogen and the aromatic ring of the backbone can be assigned to the signal at 49 ppm, in case of the nonmethylated, and 53 ppm, in case of the methylated repeat unit.

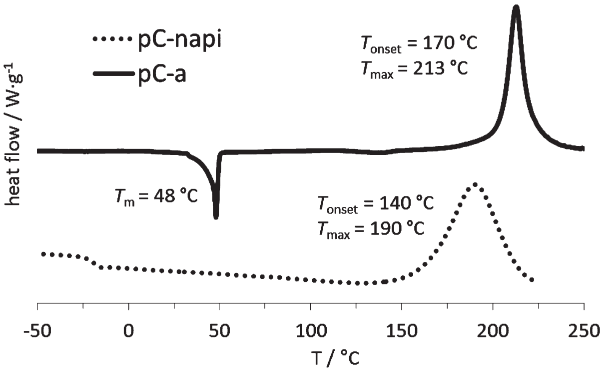


Figure 3. DSC analysis (endo down) of pC-a (solid line) and pC-napi (dashed line). The heating rates in both cases were 5 K·min^{-1}.

The peaks at 29, 34, and 162 ppm are solvent peaks.

The spectrum of *Me*PcC-napi is shown in Figure 2. Because of the second methylation side two values for the degree of methylation can be calculated. A value of 96.3% can be calculated for the methylation of the nitrogen atom in the backbone from the signals at 20 and 52 ppm. For the nitrogen atom in the imidazole ring a value of 85.9% was achieved according to the ratios of the integrals of the peaks at 20 and 35 ppm. Therefore, the polymer can be regarded as a copolymer of four different repeat units where either both, one or none of the tertiary amines are methylated. These different structures lead to slightly shifted signals that let the spectrum appear crowded. The signals at around 150 and 137 ppm can be assigned to the aromatic carbons in the backbone next to the hydroxyl group and the imidazole carbon between the nitrogen atoms. The peaks in the range of 115 to 125 ppm can be assigned to the rest of the aromatic carbons. The signals at around 25 ppm can be assigned to the second methylene group in the side chain. The methylene groups of the backbone and the methylene group of the side chain next to a charged nitrogen overlap with the signal for the methyl group of the quaternary nitrogen. The signals for the methylene groups of the side chain next to uncharged nitrogen can be found in the region of 46 ppm. The solvent peak appears at 39 ppm.

The big difference in the degree of methylation at the backbone nitrogen of *Me*PpC-napi and *Me*PpC-a can be explained by the difference in basicity. In case of *Me*PpC-a the nitrogen atom is attached to an aromatic group in contrast to PpC-napi where an alkyl chain is present. Comparing the pK_b values for *N*,*N*-dimethylaniline (pK_b = 8.9) and triethylamine (pK_b = 3.2) as a reference, the basicity of the aromatic amine is significantly weaker. Therefore, the backbone methylation can be pushed to much higher percentage in the case of PcP-napi. The pK_b of the unsaturated nitrogen in the imidazole ring can be estimated to be roughly 7. This estimation is based on the pK_b of imidazole (pK_b = 7), since its basicity is originated from the free electron pair of the unsaturated nitrogen located in the sp^2-orbital orthogonal to the aromatic ring electrons. The degree of methylation is therefore expected to reach a value somewhere between the values for the aromatic and alkyl-substituted backbone nitrogen. The experimental value of around 86% follows this theoretically derived trend.

3.2. Thermal Analysis. DSC and TGA analysis has been carried out to investigate thermal behavior of the polyelectrolytes, unmethylated polybenzoxazines as well as the starting monomers. Figure 3 shows the DSC thermograms of pC-a and

Table 2. Glass Transition Temperatures of Unmethylated Linear Polybenzoxazines Derived by DSC Analysis

sample	T_g/°C
PpC-a	72.5
PpC-napi	47.1
PpC-a/napi (1:1)	73.2

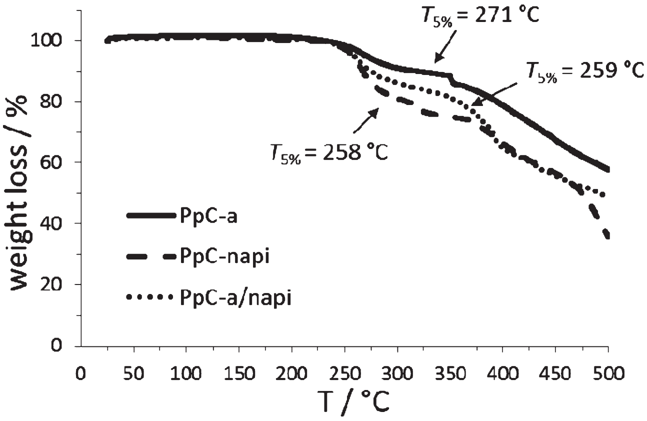


Figure 4. TGA analysis of the unmethylated linear polybenzoxazines. The heating rates were 5 K·min^{-1}.

pC-napi. The aniline based benzoxazine pC-a shows a pronounced endothermic melting peak at 48 °C due to the high crystallinity of the compound. The curing starts at 170 °C and reaches its maximum at 213 °C. The exothermic curing of pC-napi can be observed at lower temperatures with T_{onset} = 140 °C and $T_{\max}$ = 190 °C. On the basis of these results we chose the matching curing cycles.

Glass transition temperatures of the unmethylated linear polybenzoxazines have been obtained by DSC measurements (Table 2). The T_g of PpC-a of around 73 °C exceeds the value of PpC-napi by over 25 °C. The difference can be explained by the higher stiffness of the polymer chain of PpC-a caused by the aromatic benzene ring linked to the nitrogen of the backbone. In case of PpC-napi an alkyl spacer in the length of 3 methylene groups is present which links the aromatic imidazole to the backbone and results in higher chain flexibility and lowers the glass transition temperature. Interestingly, the T_g for the copolymer slightly exceeds the value of PpC-a. This is surprising, since the more flexible imidazole based monomer unit is incorporated. It can be speculated that increased hydrogen bonding due to the unsaturated nitrogen in the imidazole ring and π,π-interactions between the aromatic rings are the origin of this phenomena. The formation of exceptionally strong hydrogen bonds is a well-known characteristic of polybenzoxazines and has been already described in literature.[9]

The degradation behavior has been studied by TGA. Thermal stability is one of the key features of benzoxazines and an important property for a wide range of applications. Figure 4 shows the thermograms and the resulting $T_{5\%}$ values (weight loss reaches 5%) of the unmethylated polybenzoxazines. PpC-a can stand temperatures up to 271 °C compared to 258 and 259 °C for PpC-napi and the copolymer, respectively. The comparable values of the pC-napi based species lead to the thesis that pC-napi is the limiting factor in terms of stability.

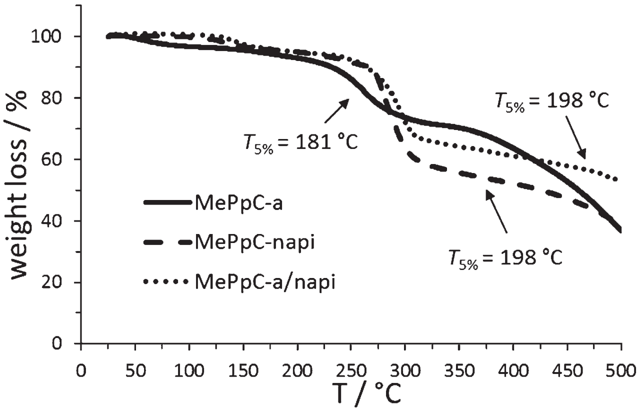


Figure 5. TGA thermograms of the polybenzoxazine polyelectrolytes. The heating rates were 5 K·min^{-1}.

Figure 5 shows the degradation behavior of the polycationic polybenzoxazines. It can be observed that the $T_{5\%}$ values drop significantly by around 60 °C in case of the imidazole containing polymers and 90 °C for PpC-a. Therefore, the thermal stability is drastically decreased.

In contrast to the thermograms of the umethylated species, the graphs of the polyelectrolytes show an irregular decrease starting at roughly 50 °C. This effect has its origin in the hygroscopicity of the samples. The samples absorb water from the atmosphere which is than evaporated during the heating process in the TGA causing unwanted deflections.

3.3. Solubility. The solubility of the different linear methylated and unmethylated polybenzoxazines in a variety of solvents has been investigated. Table 3 gives an overview of the results on a scale from insoluble to very good solubility. DMF and DMSO are able to solubilize all species. In toluene, acetone and ethyl acetate the polymers proved to be insoluble. Methanol and ethanol is able to solubilize the polyelectrolytes, whereas THF can only be used as a solvent for the nonmethylated species.

As expected, all uncharged polymers do not show water solubility. Furthermore, even *Me*PpC-a is insoluble in water. Only the pC-napi containing methylated polymers show very good water solubility. These results show that the partial methylation of the backbone nitrogen of ca. 54% in *Me*PpC-a is not sufficient to transform the polybenzoxazine into its water-soluble form. The introduction of methylated imidazole groups in the side chain in conjunction with an almost complete backbone nitrogen methylation is the key toward water solubility due to the increase in the number of charges in the macromolecule. It can be speculated that if a higher degree of methylation could be achieved for *Me*PpC-a, water-solubility is obtained.

Further solubility experiments have been carried out to detect a critical pC-a to pC-napi ratio in the copolymer *Me*PpC-a/napi up to which water-solubility is maintained (Table 4). Above the ratio of 4:1 the polyelectrolytes are insoluble in water.

On the basis of the resulting molar ratios and the estimated degrees of methylation obtained by ^{13}C NMR for the homopolymers an overall degree of methylation for the backbone and the side chain has been calculated (Table 4). For the weight ratio of 4:1 a critical degree of methylation for the backbone of 62% and 15% for the side chain is calculated. Of course, this value can only be regarded as a rough estimation since it assumes that water-solubility has its only origin in the number of charges and neglects other important interactions. On the basis of these

Table 3. Solubility of the Methylated and Unmethylated Polybenzoxazines in Different Solvents Rated on a Scale from "Insoluble" (--), "Poor" (-), and "Good" (+) to "Very Good" (++) Solubility

	PpC-a	*Me*PpC-a	PpC-napi	*Me*PpC-napi	PpC-a/napi (1:1)	*Me*PpC-a/napi (1:1)
H_2O	--	--	--	++	--	++
acetone	--	--	--	--	--	--
EtAc	--	--	--	--	--	--
MeOH	--	+	--	++	--	++
EtOH	--	-	+	+	-	+
THF	+	--	-	--	+	--
toluene	--	--	--	--	--	--
DMF	-	+	+	++	+	++
DCM	-	--	++	-	++	-
DMSO	+	+	-	+	+	+

Table 4. Solubility of *Me*PpC-a/napi Copolymers of Different pC-a/pC-napi Ratios in Water on a Scale from "Insoluble" (--), "Poor" (-), and "Good" (+) to "Very Good" (++) Solubility and the According Overall Degrees of Methylation

pC-a/pC-napi ratio[a]		0:1	1:1	3:2	7:3	4:1	9:1	1:0
H_2O		++	++	++	+	-	--	--
overall degree of methylation[b]/%	backbone	96	74	70	66	62	58	54
	side chain	86	40	32	23	15	8	0

[a] Molar ratio based on the amount of used monomer. [b] Estimated overall degree of methylation based on the experimentally calculated degree of methylation of the homopolymers (0:1 and 1:0).

results, a backbone alkylation of over 60% is necessary to obtain water-solubility. The other 40% of the backbone groups is therefore still available for the formation of hydrogen bonds that have proven to be of major importance in polybenzoxazine chemistry.[17−20]

Please note that the already mentioned unique hydrogen bonding capabilities of 1,3-benzoxazine-based polymers are a structure inherent property and are fundamentally maintained even in the solubilized state. To our knowledge our contribution in addition with a recently published patent[21] describes for the first time that a partial polymer analogous alkylation reaction can be used for adjusting the solubility of *N*-alkyl and *N*-aryl type polybenzoxazine derivatives in various solvents including water. Especially the non-modified repeat units due to the partial nitrogen quarternization degree throughout the polymer structure are expected to provide specific interactions in environments, which are typically not accessible to polybenzoxazines. For example novel dye-transfer inhibition properties, as desired for anticolor transfer detergents, were already observed in aqueous media.[21] It shall be emphasized that this property relies fundamentally on intermolecular dye−polymer interactions.[22] Especially for this application the polycationic nature of our novel polybenzoxazine derivatives supports in a synergistic manner the adhesion to a variety of important substrates, including polyesters, polyamides or wool. In conjunction with the great design flexibility of polybenzoxazines the (partial) alkylation therefore offers a versatile pathway to a novel polyelectrolyte class of adjustable solubility and unique hydrogen bonding capabilities.

4. CONCLUSIONS

Different polyelectrolytes have been obtained by a polymer analogous reaction of linear polybenzoxazines. In a first step, different linear homopolymers and copolymers of the monomers 3,4-dihydro-6-methyl-3-phenyl-2*H*-1,3-benzoxazine (pC-a) and 3-[3-(1*H*-imidazole-1-yl)propyl]-6-methyl-3,4-dihydro-2*H*-1,3-benzoxazine (pC-napi) have been synthesized by thermal ring-opening polymerization. In a second step, cationic polyelectrolytes have been obtained by methylation of the tertiary backbone nitrogen and, in case of the pC-a based species, the nitrogen of the imidazole ring.

^{13}C NMR experiments allowed the calculation of a degree of methylation for the individual methylation sides. Depending on the basicity of the according nitrogens, values of around 54% for the backbone nitrogen of the pC-a-based polybenzoxazine, 96% for the backbone nitrogen of the pC-napi-based polybenzoxazine, and 86% for the nitrogen of the imidazole ring have been achieved.

TGA experiments revealed that methylation decreases the temperature stability by 60 to 90 °C leading to $T_{5\%}$-values of 181 °C for the pC-a-based homopolymer and 198 °C for pC-napi-based polymers.

Special focus was lead on the solubility behavior of the different polymers in various solvents especially water. The partial methylation of 54% did not lead to water-soluble polyelectrolytes. A series of PpC-a/PpC-napi copolymers of different repeating unit ratios has been investigated to derive a critical degree of methylation necessary to obtain water-soluble polymers. A backbone methylation of over 60% in combination with a side chain methylation of about 15% turned out to be the key toward water-solubility. The unique capability for the formation of hydrogen bonding, an important characteristic of polybenzoxazines, is maintained due to the presence of unmethylated nitrogen atoms in the polymer.

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■ REFERENCES

(1) Jaeger, W.; Bohrisch, J.; Laschewsky, A. *Prog. Polym. Sci.* **2010**, *35* (5), 511–577.

(2) Terminology of Polymers Containing Ionizable or Ionic Groups and of Polymers Containing Ions (2006). In *Compendium of Polymer Terminology and Nomenclature: IUPAC RECOMMENDATIONS 2008*, Jones, R. G., Kahovec, J., Stepto, R., Wilks, E. S., Hess, M., Kitayama, T., Metanomski, W. V., Eds.; The Royal Society of Chemistry: London, 2009; pp 205−210.

(3) Dragan, E.; Ghimici, L. Nitrogen based synthetic polycations. Syntheses and applications. In *Focus on Ionic Polymers*, Dragan, E., Ed. Research Signpost: Trivandrum, Kerala, India, 2005; pp 1—48.

(4) Noguchi, H., *Ionene Polymers*. In Salomone, J. C., Ed. CRC Press: London, New York, Tokyo, 1996.

(5) Demir, K. D.; Tasdelen, M. A.; Uyar, T.; Kawaguchi, A. W.; Sudo, A.; Endo, T.; Yagci, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2011**in press.

(6) Ishida, H.; Agag, T., *Handbook of Benzoxazine Resins*. Elsevier: 2011.

(7) Ghosh, N. N.; Kiskan, B.; Yagci, Y. *Prog. Polym. Sci.* **2007**, *32* (11), 1344–1391.

(8) Kimura, H.; Matsumoto, A.; Hasegawa, K.; Ohtsuka, K.; Fukuda, A. *J. Appl. Polym. Sci.* **1998**, *68* (12), 1903–1910.

(9) Ishida, H.; Lee, Y.-H. *J. Appl. Polym. Sci.* **2002**, *83* (9), 1848–1855.

(10) Sawaryn, C.; Landfester, K.; Taden, A. *Macromolecules* **2010**, *43* (21), 8933–8941.

(11) Sawaryn, C.; Landfester, K.; Taden, A. *Polymer* **2011**, *52* (15), 3277–3287.

(12) Sawaryn, C.; Landfester, K.; Taden, A. *Macromolecules* **2011**, *44* (14), 5650–5658.

(13) Rimdusit, S.; Ishida, H. *Polymer* **2000**, *41* (22), 7941–7949.

(14) Liu, C.; Shen, D.; Sebastián, R. M. a.; Marquet, J.; Schönfeld, R. *Macromolecules* **2011**, *44* (12), 4616–4622.

(15) Chirachanchai, S.; Laobuthee, A.; Phongtamrug, S. *J. Heterocycl. Chem.* **2009**, *46* (4), 714–721.

(16) Riess, G.; Schwob, L. J.; Guth, G.; Roche, M.; Lande, B. Ring opening polymerization of benzoxazines—A new route to phenolic resins. In *Advances in polymer synthesis*; Culbertson, M. B., McGrath, E. J., Eds.; Plenum Press: New York, 1985; Vol. 31.

(17) Schnell, I.; Brown, S. P.; Low, H. Y.; Ishida, H.; Spiess, H. W. *J. Am. Chem. Soc.* **1998**, *120* (45), 11784–11795.

(18) Dong, H. J.; Xin, Z.; Lu, X.; Lv, Y. H. *Polymer* **2011**, *52* (4), 1092–1101.

(19) Ishida, H.; Lee, Y. H. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39* (7), 736–749.

(20) Liao, C. S.; Wang, C. F.; Lin, H. C.; Chou, H. Y.; Chang, F. C. *J. Phys. Chem. C* **2008**, *112* (42), 16189–16191.

(21) Taden, A.; Kreiling, S.; Schoenfeld, R.; Barreleiro, P.; Eitin, T. Cationic benzoxazine (co)polymers. *WO 2010/130626*, 06.05.2010, 2009.

(22) Oakes, J.; Dixon, S. *Rev. Prog. Color. Relat. Top.* **2004**, *34* (1), 110–128.