Thermoresponsive Poly(2-oxazoline) Molecular Brushes by Living Ionic Polymerization: Kinetic Investigations of Pendant Chain Grafting and Cloud Point Modulation by Backbone and Side Chain Length Variation

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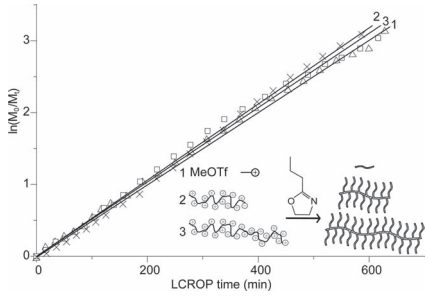
Molecular brushes of poly(2-oxazoline)s were prepared by living anionic polymerization of 2-iso-propenyl-2-oxazoline to form the backbone and subsequent living cationic ring-opening polymerization of 2-*n*- or 2-*iso*-propyl-2-oxazoline for pendant chain grafting. In situ kinetic studies indicate that the initiation efficiency and polymerization rates are independent from the number of initiator functions per initiator molecule. This was attributed to the high efficiency of oxazolinium salt and the stretched conformation of the backbone, which is caused by the electrostatic repulsion of the oxazolinium moieties along the macroinitiator. The resulting molecular brushes showed thermoresponsive properties, that is, having a defined cloud point (CP). The dependence of the CP as a function of backbone and side chain length as well as concentration was studied.



1. Introduction

Molecular brushes are linear macromolecules with pendant polymer side chains at high grafting densities, ideally at each backbone monomer unit.[1] The side chain crowding induces a strong stretching of the backbone and the polymer side chains, and the entire molecular brush adopts an entropically unfavorable elongated cylindrical or worm-like shape.[2] Because of their unique structure, molecular brushes exhibit some novel properties and are discussed for potential applications as sensors,[3] elastomers,[4] actuators[5] as well as unimolecular templates for nanowires.[6–8]

Since the pioneering work by Tsukahara et al.[9] and the first report by Schmidt,[2,10] molecular brushes have intrigued researchers in the preparation and investigation of molecular brushes with various architectures and compositions. One focus of the research on molecular brushes is the development of stimuli responsive systems.[11] In particular, the thermoresponsive molecular brushes[12–16] with a lower critical solution temperature (LCST) in aqueous environments have been extensively explored because of their intriguing potentials in, for example, biomedical fields.[17–19]

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As linear polymers, the LCST of molecular brushes can be modulated by, for example, their composition, molecular weight, or the concentration.[14,15] However, as a special polymer class, the LCST of molecular brushes can also be modulated by the side chain composition, end groups, and grafting density.[14,20–24] It should be noted that, unlike linear polymers, molecular brushes may collapse as individual molecules in a solvent with a low surface tension[25] or even at temperatures above the LCST of the linear analog.[5,13,26]

For instance, Schmidt and co-workers[5] prepared molecular brushes with poly(*N*-isopropylacrylamide) (PNIPAAm) side chains by grafting from a defined macroinitiator using atom-transfer radical polymerization (ATRP). The resulting PNIPAAm brushes collapsed in the aqueous solution as the LCST of the PNIPAAm side chains was reached. These materials were shown to experience a conformational transition from a single macromolecule cylinder to a sphere within an extremely small temperature range. Later, Matyjaszewski and co-workers[13] reported on an unusual concentration-dependent aggregation behavior of molecular brushes in aqueous solution. Because of the compact structure, intramolecular collapse rather than intermolecular aggregation occurred when the average distance between brush molecules is much larger than the hydrodynamic dimensions of the individual macromolecules. However, at higher concentrations, when the distance between brush molecules is comparable to the brush hydrodynamic dimensions, intermolecular aggregation mainly occurred, which is typical for linear thermoresponsive polymers in solution. The structural motif of molecular brushes is also a common for biomacromolecules. The most prominent examples are proteoglycans, a major component of the extracellular matrix and present on the cell surface of every adhered cell. Among their multiple and very diverse (partially still unknown) functions, they play a significant role in cell adhesion, motility, proliferation, stem cell differentiation, and tissue morphogenesis and later determine the mechanical strength of tissue.[27–30] Hence, specifically tailored hydrophilic synthetic molecular brushes have a biomimetic potential to modulate cell adhesion and tissue properties and are in the focus of biomaterials research.

Recently, hydrophilic and non-toxic poly(2-oxazoline)s (POx) came into the focus of biomaterials research as a good alternative to the established poly(ethylene glycol) (PEG) systems.[31–42] Unlike PEG, the pseudo-polypeptide structure of POx and synthetic variability renders it as a suitable polymer to tailor biomimetic systems. The living cationic ring-opening polymerization (LCROP) of 2-substituted 2-oxazolines allows for the synthesis of defined macromolecules with a broad variety of architectures, composition, side and end functionalities.[43–53] Moreover, the LCST of POx can be adjusted over a broad temperature range.[54–62]

Recently, we reported on the synthesis of molecular brushes by the *grafting-from* method via LCROP of 2-alkyl-2-oxazolines from a polycationic macroinitiator, that is, from the poly(2-oxazolinium) salt.[16] The resulting molecular brushes showed sharp, reversible transition temperatures in aqueous solutions without noticeable hysteresis and a distinct self-aggregation.[63] Moreover, as linear POx, the LCST of their molecular brush or comb-polymer analogs can be tuned by the variation of the side chain composition and end groups in a wide range (4–90 °C).[16,64] POx-based molecular brushes can also be prepared on various surfaces resulting in so-called bottle-brush brushes (BBBs).[65] The synthetic possibilities of the LCROP forming the pendant chains can be used for the design of surface bound biosensors, with BBBs bearing specific pendant polymer end-functions for charge transport[66] and large functional biomolecules.[67] Recently, POx brushes were also successfully used to control protein adsorption, as well as bacteria and cell adhesion.[36,68,69] Their non-fouling properties are at least equal to coatings based on PEG brushes[70–73] but might be more suitable for long term use as POx cannot undergo oxidative degradation and do not complex ions.[74–76] Regarding the unique molecular structure and the potential application as biomaterials, a conclusive study of the synthetic possibilities and the structure-LCST relationship of POx-based molecular brushes is needed.

In this report, we address the synthetic aspects of molecular brush formation by the *grafting-from* method using only living ionic polymerization reactions to construct structurally defined stem and pendant chains. In situ kinetic studies of the side chain grafting by LCROP from (macro)initiators of increasing molar mass and functionality were performed to elucidate the initiation efficiency of oxazolinium moieties along the macroinitiators and side chain growth LCROP. Moreover, the influence of side chain length on the cloud point (CP) and conformation of molecular brushes was investigated.

2. Experimental Section

2.1. Materials

All chemicals were purchased from Sigma–Aldrich (Steinheim, Germany) or Acros (Geel, Belgium) and used as received unless otherwise stated. Acetonitrile (ACN), methyl triflate (MeOTf), 2-methyl-2-oxazoline (MeOx), 2-*iso*-propyl-2-oxazoline (*i*POx), 2-*n*-propyl-2-oxazoline (*n*POx), and 2-isopropenyl-2-oxazoline (IPOx) were refluxed over CaH_2 and distilled under Argon prior to use. The monomers *n*PrOx, *i*PrOx, and macroinitiators were prepared according to procedure published before.[16]

2.2. Analysis

Gel permeation chromatography (GPC) was performed on a Waters system (pump mod. 510, RI-detector mod. 410) using Resi Pore Guard (50 × 7.5 mm) and 2 × Resi Pore (300 × 7.5 mm) columns as the stationary and dimethyl acetamide (DMAc) (58 mmol L^{-1} LiBr, T = 80 °C, 1 mL min^{-1}) as the mobile phase. The calculation of the average molar mass was performed using a calibration with PMMA standards from PSS (Mainz, Germany). Prior to the measurements, the polymer samples were dissolved in DMAc and filtered through 0.2 μm PTFE filters. Gas chromatography (GC) was performed on a Varian CP 3380 equipped with a CombiPal and with a Nordion NB-54 column (25 m, 0.20 mm, 0.25 μm) and FID detector (helium carrier gas). Turbidity measurements were carried out on a Cary 3 UV–vis spectrophotometer from Varian. The CP was determined by spectrophotometric detection of the changes in transmittance at λ = 500 nm of the aqueous polymer solutions (1.0 wt% unless otherwise stated). The heating/cooling rate was 1.0 °C min^{-1} followed by a 5 min period of constant temperature to ensure equilibration. Given values for the CP were determined as the temperature corresponding to a 10% decrease in optical transmittance.

2.3. Anionic Polymerization: Poly(2-isopropenyl-2-oxazoline) ($PIPOx^{I}$, $PIPOx^{II}$, and $PIPOx^{III}$)

Adapting our recent report on the preparation of molecular brushes,[16] three PIPOx polymers with different molar masses were prepared, that is, $PIPOx^{I}$: $\overline{M}_n$ = 5.8 kg mol^{-1}, $Đ = \overline{M}_w/\overline{M}_n$ = 1.12; $PIPOx^{II}$: $\overline{M}_n$ = 14.7 kg mol^{-1}, $Đ = \overline{M}_w/\overline{M}_n$ = 1.21; **$PIPOx^{III}$**: $\overline{M}_n$ = 24.0 kg mol^{-1}, $Đ = \overline{M}_w/\overline{M}_n$ = 1.20.

^{1}H NMR ($CDCl_3$): δ (ppm) = 4.16 (br, 2H, —O—CH_2—CH_2—N=), 3.76 (br, 2H, —O—CH_2—CH_2—N=), 1.86–1.75 (br, 2H, —C—CH_2—), 1.24–1.14 (br, 3H, —C—CH_3) and 0.85 (br, C_4H_9).

2.4. Macroinitiator Salt: Poly(2-isopropenyl-2-oxazolinium triflate) (M^{I}, M^{II}, and M^{III})

The three macroinitiators M^{I} (short), M^{II} (middle), and M^{III} (long) were prepared according the procedure we published before. Briefly, under argon atmosphere, PIPOx (222 mg, 1.0 equiv of oxazoline unit) and 394 mg (2.4 mmol, 1.2 equiv) of MeOTf were added to 5 mL dry acetonitrile at approximately −35 °C. After stirring for 5 h at 0–5 °C, the mixture was poured into cold and dry diethyl ether to precipitate the oxazolinium salt. The precipitate was washed twice with cold ether to yield 529 mg colorless compound (1.92 mmol, 96%).

^{1}H NMR (CD_3CN): δ (ppm) = 5.08 (br, 2H, —N—CH_2—CH_2—O—), 4.54 (br, 2H, —N—CH_2—CH_2—O—), 3.70 (s, 3H, CH_3 —N), 2.49 (2H, —C—CH_2—) and 1.36 (br, 3H, —C—CH_3)

2.5. Poly(2-*iso*-propenyl-2-oxazoline-g-2-*n*-propyl-2-oxazoline) (MB^{I}-1 – MB^{I}-3, and MB^{II}-1 – MB^{II}-4)

At 0 °C, M^{I} or M^{II} (44 mg, 0.16 mmol, 1.0 equiv.) was dissolved in 4 mL of acetonitrile and 452 mg of *n*PrOx (4.0 mmol, 25 equiv.) was added to the solution. The polymerization was performed at 80 °C. Samples from the reaction mixture were taken periodically for monomer conversion (GC) and molar mass (GPC) measurement. The polymerization was terminated by addition of excess of piperidine. After stirring the reaction mixture for 8 h at room temperature, an excess of finely grounded potassium carbonate (≈60 mg) was added and the mixture was allowed to stir overnight. The solvent was removed under reduced pressure and the residual dissolved in chloroform and then precipitated three times in dry diethyl ether. The product was freeze-dried (water) to yield a colorless powder. Additionally, the product was purified by column chromatography using Sephadex G100 to quantitatively separate the product from minor portions of homopolymer side products.

^{1}H NMR ($CDCl_3$): δ (ppm) = 3.44 (br, 93 H, —N—(CH_2)$_2$—N), 2.33/2.20 (m, 48 H, —CO—CH_2—CH_2—CH_3), 1.62 (br, 51 H, —CO—CH_2—CH_2—CH_3) and 0.94 (br, 75 H, —CO—CH_2—CH_2—CH_3).

Poly(2-isopropenyl-2-oxazoline-g-2-*iso*-propyl-2-oxazoline) (MB^{I}-4, MB^{II}-5 – MB^{II}-7 and MB^{III}-1) were synthesized according to the above procedure.

^{1}H NMR ($CDCl_3$): δ (ppm) = 3.45 (br, 76H, —N—CH_2—CH_2—N—), 2.88 (br, 23H, —CO—CH(CH_3)$_2$), 1.98/1.92 (br, 2H, —CH_2—C), 1.45 (br, 3H, —CH_3—C) and 1.09 (br, 110H, —CH(CH_3)$_2$).

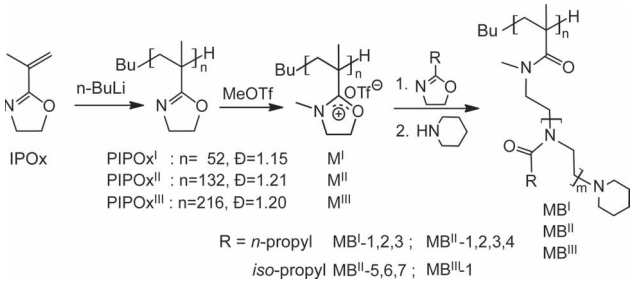
2.6. In Situ Kinetics Studies by On-Line Gas Chromatography

For the kinetic measurements, the polymerization mixtures were prepared and sealed in a glove-box under an inert and dry atmosphere in a crimp-vial. The GC agitator was preheated to the indicated temperature. The CombiPal was programmed for two syringe wash cycles (ACN) prior and after sampling. The sealed reaction container was introduced to the agitator immediately (approx. 1 s) before the first sampling, in order to obtain a zero-time value. Per injection, 2 μL of the reaction mixture was taken. The monomer consumption was followed by the change of the ratio of the integrals of the monomer and the internal standard (chlorobenzene). All polymerization reactions were carried out in dry ACN as solvent at 80 °C. The typical procedure is as follows: To a solution of 4.0 mL ACN and 44 mg of macroinitiator (or 26.3 mg of methyl triflate) (0.16 mmol, 1 equiv.), 452 mg (4.0 mmol, 25 equiv.) *n*PrOx or *i*PrOx and 0.2 mL chlorobenzene (inner standard) were added at 0 °C and the vial was sealed. To start the polymerization, the vial was inserted to the preheated agitator unit of the GC at 80 °C.

3. Results and Discussion

3.1. Synthesis

Three defined polymers poly(2-isopropenyl-2-oxazoline), ($PIPOx^{I}$, $PIPOx^{II}$, and $PIPOx^{III}$) forming the molecular brush backbone were prepared by living anionic polymerization of 2-isopropenyl-2-oxazoline (IPOx).[16] End group analysis (see Figure SI1, Supporting Information) based on ^{1}H NMR spectroscopic data and GPC gave a degree of polymerization, n, for $PIPOx^{I}$ of n = 52 with a very narrow dispersity ($Đ$) of 1.15, for $PIPOx^{II}$ of n = 132 with a slightly broader



Scheme 1. Reaction scheme for the preparation of molecular brushes of poly(2-oxazoline)s (POx). Synthesis of the molecular brush backbone by living anionic polymerization of 2-isopropenyl-2-oxazoline (IPOx), followed by conversion to the macroinitiator and formation of side chains by living cationic ring-opening polymerization of 2-*n*-propyl (*n*PrOx) and 2-*iso*-propyl-2-oxazoline (*i*PrOx) and termination with piperidine.

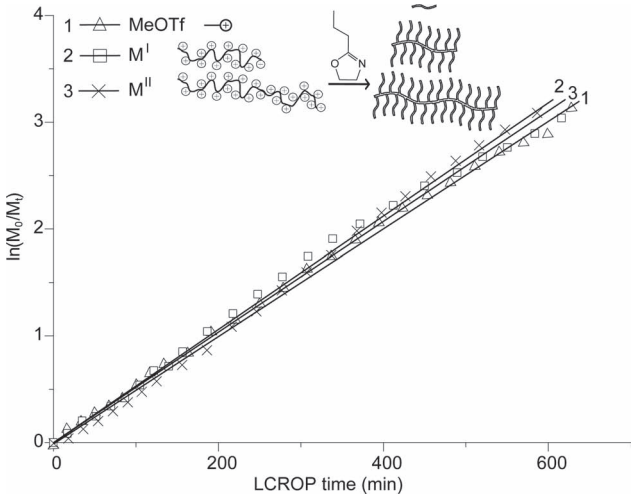


Figure 1. First-order kinetic plots for the grafting polymerization of 2-*n*-propyl-2-oxazoline in the presence of monofunctional MeOTf (1) and plurifunctional macroinitiators M^{I} (2) and M^{II} (3).

dispersity ($Đ$) of 1.21 and n = 216 with a dispersity of $Đ$ = 1.21 for PIPOx^{III}, respectively. As outlined in Scheme 1, the consecutive reaction with stochiometric amounts of methyl triflate (MeOTf) yield the polycationic macroinitiators M^{I}, M^{II}, and M^{III} for side chain formation by the *grafting-from* approach by means of LCROP.[77–80] In accordance to our previous account, the conversion from PIPOx backbone to the macroinitiator salt was with at least 98.5% almost quantitative as calculated from the ^{1}H NMR spectroscopic data.

3.2. Side Chain Grafting kinetics by LCROP

Kinetic investigations of the LCROP using either methyl trifluorosulfonate (MeOTf) or the macroinitiators M^{I} and M^{II} were performed using 2-*n*-propyl-2-oxazoline (*n*PrOx) to evaluate whether all initiators initiate the polymerization in an analog manner. To compare the polymerization kinetics of single and multifunctional initiators, one possible way is to compare the apparent polymerization rate.[51] However, for the oxazolinium macroinitiator, the apparent polymerization rate is not reliable due to the somewhat inaccurate determination of molar mass of the hygroscopic macroinitiator. Thus, we compared the apparent polymerization rate per initiating group as it can be determined more accurately. The LCROP of *n*PrOx at an initial concentration of $[n\text{PrOx}]_0$ = 1.0 mol L^{-1} in the presence of MeOTf, M^{I}, and M^{II} were conducted at 80 °C. For all reactions, the oxazolinium unit concentrations for MeOTf, M^{I}, and M^{II} were kept constant to $[I]_0$ = 0.04 mol L^{-1}, which calculates to an initial monomer to initiator ratio of $[M]_0/[I]_0$ = 25. For all grafting reactions, a pseudo-first order kinetic behavior was found. As apparent from Figure 1, all three plots are linear, indicating a living character of the cationic polymerization with no noticeable termination reactions even to very high monomer conversion (>95%). For all three reactions, the polymerization proceeded to quantitative monomer conversions. Furthermore, the slopes of the plots are virtually identical, regardless of the length and (poly)functionality of the (macro)initiator. The apparent polymerization rates per initiating group were calculated to be 2.18, 2.12, and 2.08 mL s^{-1}·mol^{-1} for M^{I}, M^{II}, and MeOTf, respectively (Table 1). The minor but noticeable differences are within the experimental error of the GC measurement.

This indicates that regardless of the initiator site crowding and number of the initiation sites (1, 52, or 132), the LCROP-grafting from reaction proceeds at the same initiation and polymerization rate for each initiator function. In a second set of experiments, a more bulky monomer was grafted. For 2-*iso*-propyl-2-oxazoline (*i*PrOx), the LCROP with MeOTf and M^{II} as the initiator was studied. The apparent polymerization rates per initiating group were found to be very similar and calculate to 1.25 for MeOTf and 1.28 mL s^{-1} mol^{-1} for M^{II}. Hence, our findings above for *n*PrOx, the findings on the grafting for *i*PrOx and also earlier observations on 2-oxazoline side chain grafting[16] as well as grafting from small plurifunctional initiators[51] strongly indicates that the LCROP-grafting reaction of 2-oxazoline using oxazolinium macroinitiators results in an uniform initiation and propagation reaction that give molecular brushes with POx pendant chains of high grafting density and of equal length. Surprisingly, no significant difference of the reaction kinetics was found between the single MeOTf initiator and the plurifunctional macroinitiators (M^{I}, M^{II}). We attribute the undisturbed initiation of each initiator function along the macroinitiator chain to its polycationic nature that causes significant chain stretching and hence good accessibility

Table 1. Calculation of apparent polymerization rates per initiating group using *n*PrOx and different initiators.

Initiator	Degree of functionalization[a)]	Monomer	$[M]_0/[I]_0$	k_p [mL S^{-1} mol^{-1}]
MeOTf	100%	*n*PrOx	25/1	2.08
M^I	98%	*n*PrOx	25/1	2.18
M^{II}	98.5%	*n*PrOx	25/1	2.12
M^{II}	98.5%	*i*PrOx	25/1	1.28
MeOTf	100%	*i*PrOx	25/1	1.25

[a)]Determined by ^{1}H NMR spectroscopy.

of each initiator site and to the known high reactivity of oxazolinium salts[78] being similar to alkyl triflates.[16,51,52]

Following the kinetic studies, the macroinitiators M^I and M^{II} were used to synthesize sets of molecular brushes (MB^I and MB^{II}) with *n*PrOx and *i*PrOx side chains. In order to obtain a homologue series of molecular brushes, we took advantage of the highly living nature of the LCROP side chain grafting reaction. In acetonitrile, macroinitiators M^I or M^{II} and *n*PrOx or *i*PrOx as the monomers were mixed at a ratio of 1:25 with respect to the initiator function and LCROP was started. From the ongoing LCROP, aliquots of the reaction mixture (1.0 mL) were collected after certain polymerization times and immediately terminated with an excess of piperidine (0.2 mL) and purified to result in molecular brushes (MB^I-1 to -3 and MB^{II}-1 to -7) having increasing pendant chain lengths. The analytical data for the macroinitiators and the resulting molecular brushes are given in Table 2.

For all grafting polymerizations, a steady increase of the average molar mass of the molecular brushes was found. Moreover, the GPC analysis gave monomodal and narrow distributions ($Đ$ = 1.14–1.30) for all molecular brushes. Again, the bulkiness of the used monomer (*i*PrOx vs *n*PrOx) does not seem to have an influence on the definition of the resulting molecular brush structure, even if a long macroinitiator was used. This corroborates our observations by the GC kinetic measurements that the LCROP grafting reaction is efficient and of highly living nature. Exemplarily, the GPC elugrams of the synthesized MB^{II}-1 to MB^{II}-4 from M^{II} as the macroinitiator and *n*PrOx as the monomer are shown in Figure 2. It should be noted that the $\overline{M}_n$ determined by GPC is somewhat lower than the theoretical values especially for molecular brushes with long side chains. This is due to the compact structure of molecular brushes as compared with linear, random coils of the standard polymer used for GPC calibration (PMMA) and consistent with previous reports.[14,15]

3.3. Thermoresponsive Behavior

Both theoretical simulation and experiments have shown that the conformation and solution behavior of molecular brushes can be significantly influenced by the variation of the rigidity of backbone and side chains,[21] the pendant chain grafting density,[20,81] and length.[24] To date, there is still no conclusive relation between, for example, side chain or backbone length and the thermoresponsiveness (LCST behavior) other than the relation of the total mass with the CP. To determine the influence of the molecular brush architectural parameters and composition on the CP of POx-based molecular brushes, we performed temperature dependant turbidity measurements using a 1.0 wt% aqueous solution for molecular brushes under variation of side chain and backbone chain length following a previously reported protocol.[16,59,60]

For all molecular brushes with P*n*PrOx (MB^I-1 to-3 and MB^{II}-1 to -4) or P*i*PrOx side chains (MB^I-4, MB^{II}-5 - MB^{II}-7 and MB^{III}-1), the soluble–insoluble transition was found to occur in a very narrow temperature interval (Figure 3) and without a significant hysteresis for the heating and cooling curves as POx is lacking H-donor groups. In agreement with earlier observations for linear POx, CPs of polymer from *i*PrOx are much higher than those derived from *n*PrOx. Figure 3b depicts the CP with increasing backbone length. As expected, the CP decreases monotonically with the increasing molar mass of the molecular brush. Also a compound with the same side chain (*i*PrOx) but a PIPOx backbone prepared by free-radical polymerization as reported earlier[16] fits nicely into this row, although the dispersity is significantly higher ($Đ$ = 1.58).

However, the development of the CP as a function of side chain length as shown in Figure 3a gives a very different picture. For a given backbone length (n = 132, MB^{II}-1 to MB^{II}-4) the molar mass is steadily increasing with increase of the side chain length (m = 3 to 24), however, the CP is not monotonically decreasing but shows a minimum. For very short side chains (MB^{II}-1), a CP at 23.8 °C was determined, which is in agreement with previous reports of the LCST behavior of linear P*n*PrOx of comparable molar mass (above 1.6×10^4 g mol^{-1}).[58,61] However, a slight increase of the side chain length to m = 6 results in a dramatic decrease of the CP to 19.2 °C and further doubling of the side chain length to m = 11 decreases the CP further, but only by one degree. Interestingly, for

Table 2. Analytical data of the backbone polymers (PIPOx^{I}, PIPOx^{II}, and PIPOx^{III}) and the respective molecular brushes (MB^{I}, MB^{II}, and MB^{III}) along with the determined cloud points (CP).

	Initiator	LCROP time [h]	Monomer	Conversion [%][b]	n[a]	m[c]	$\overline{M}_n$ [kg mol^{-1}][d]	$Đ$[d]	CP [°C][e]
PIPOx^{I}		–		–	52		5.8	1.15	–
MB^{I}-1	M^{I}	1	*n*PrOx	22	52	6	16.4	1.18	19.5
MB^{I}-2		2		42	52	11	27.3	1.17	18.1
MB^{I}-3		8		98	52	24	40.7	1.14	19.2
MB^{I}-4		24	*i*PrOx	97	52	24	42	1.18	31
PIPOx^{II}		–		–	132	–	14.6	1.21	–
MB^{II}-1	M^{II}	0.5	*n*PrOx	11	132	3	25.8	1.26	24
MB^{II}-2		1		22	132	6	46.2	1.23	19.2
MB^{II}-3		2		42	132	11	63.0	1.28	18.2
MB^{II}-4		8		97	132	24	102	1.30	19.2
MB^{II}-5		1.3	*i*PrOx	19	132	4	35.1	1.24	29
MB^{II}-6		3		40	132	10	48.5	1.24	28.1
MB^{II}-7		24		99	132	24	86.9	1.24	29.1
PIPOx^{III}		–		–	216	–	24.0	1.20	–
MB^{III}-1	M^{III}	24	*i*PrOx	98	216	24	125	1.33	27

[a]Degree of polymerization as determined by end-group analysis based on ^{1}H NMR spectroscopy; [b]As calculated by GC measurement; [c]Degree of polymerization of the side chains calculated from GC; [d]Dispersity $Đ = \overline{M}_w/\overline{M}_n$ calculated from GPC elugram; [e]Determined by turbidity measurements of a 1.0 wt% aqueous polymer solution (heating).

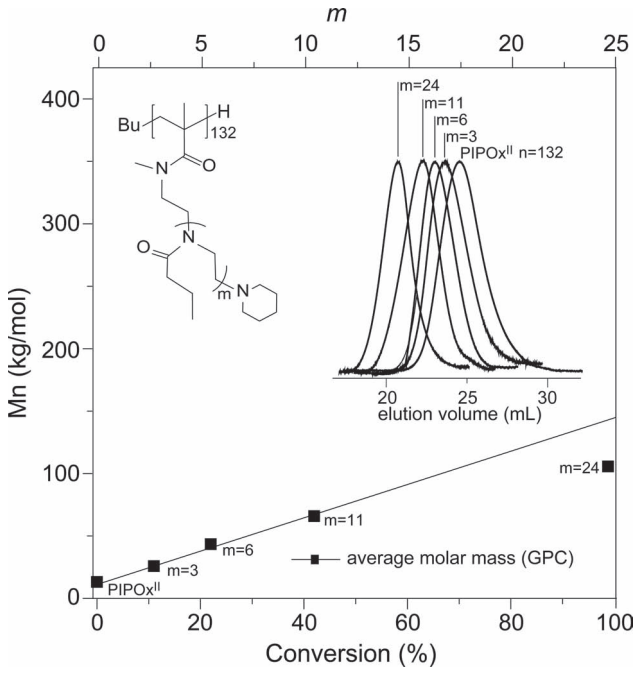


Figure 2. Plot of $\overline{M}_n$ of molecular brushes using macroinitiator M^{II} as a function of monomer conversion (2-*n*-propyl-2-oxazoline) and the degree of polymerization of side chains, *m*, as determined by GC. Inset: Gel permeation chromatography elugrams of the corresponding polymers.

m = 24, a slight increase of the transition temperature to 19.2 °C was found. The similar CP of molecular brushes with the linear analog is explainable by the fact that for very short side chains, the molecular brushes can collapse as a random coil. The increase of the side chain length influences strongly the conformational freedom of the molecular brush and thus results in the significant downshift of the CP. Further increase of the side chain length then results in the modulation of the CP of a polymer having a typical molecular brush character, which can no longer collapse to a random coil because of side chain crowding. The same development of a minimum CP with increase of the side chain length was also found for the molecular brushes (MB^{I}-1 to -3) derived from the shorter macroinitiator, M^{I} and for MB^{II}-5 to -7 with *i*PrOx side chains (see Table 2). However, the influence is not as significant because of the slightly longer minimum side chain (m = 4) and the higher steric demand of the pendant chain monomer units.

These findings are also corroborated by earlier theoretical studies by Saariaho et al.[24] They used Monte Carlo simulations to describe the change of the conformational freedom and, in consequence, the lyotropic behavior of molecular brushes with increasing side chain length, thus the transition from random coil behavior to molecular brush characteristics.

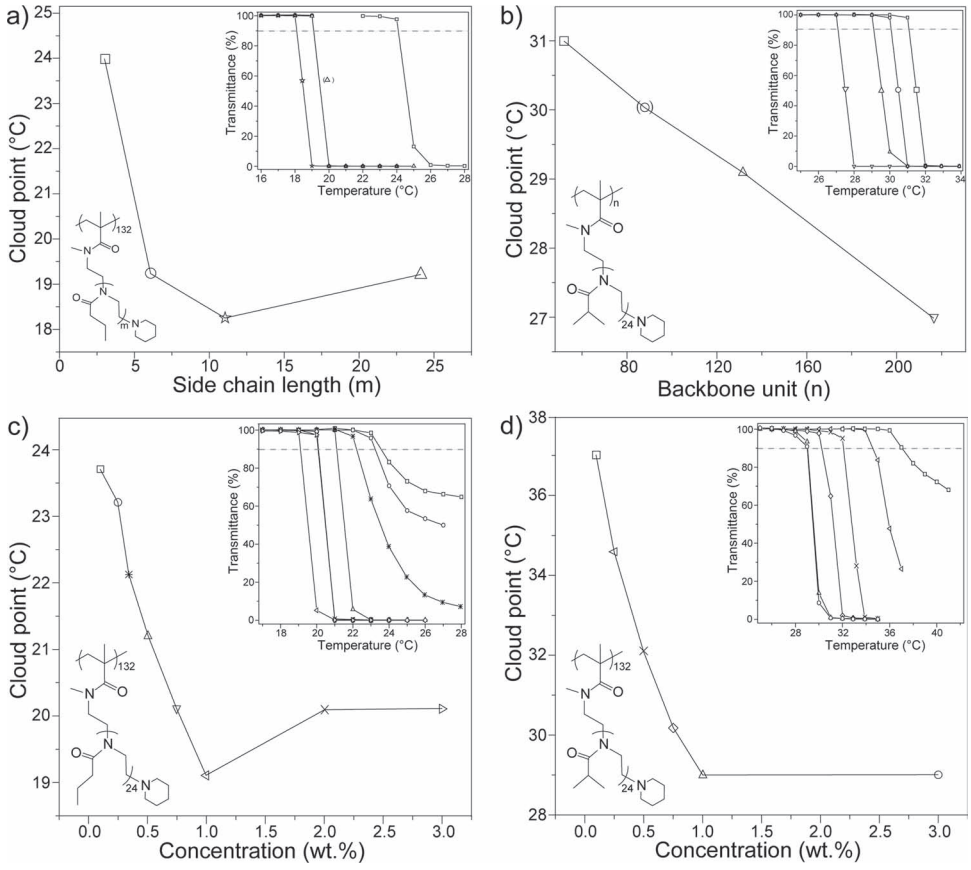


Figure 3. a) Cloud points (CP) as a function of the side chain length (MB^{II}-1 to MB^{II}-4 with $m = 3$ to 24) at a concentration of 1.0 wt%. Please note that the curves for $m = 6$ and 24 are superimposed. b) Cloud points of molecular brushes as a function of the PIPOx backbone length (n) and *i*PrOx side chains with $m = 24$ at a concentration of 1.0 wt%. (from left to right: MB^{I}-4, PIPOx prepared by free radical polymerization (ref. [16]), $n = 88$, $m = 18$ ($Đ = 1.58$), MB^{II}-7, MB^{III}-1). c) Cloud points of MB^{II}-4 as a function of the concentration (0.1 to 3.0 wt%). d) Cloud points of MB^{II}-7 as a function of the concentration (0.1 to 3.0 wt%). Insets a)–d): Related turbidity measurements of the aqueous solutions (heating).

In Figure 3c, the CPs of MB^{II}-4 at concentrations from 0.1 to 3.0 wt% are shown. With increasing concentration, the CPs linearly decreases from 24 °C to 19.1 °C. Further increase of the concentration had only little effect on the CP value and was found to level around 20 °C, thus the LCST) of this molecular brush is around 19 °C. A similar behavior was found for MB^{II}-7 with the same backbone and side chain length but with P*i*PrOx pendant chains. Here, the LCST was found to be 29 °C, thus around 10 °C higher as the structurally related molecular brush with P*n*POx side chains.

4. Conclusions

Polycationic macroinitiators of different length were prepared by living anionic polymerization of 2-isopropenyl-2-oxazoline. In situ kinetic studies of side chain grafting by LCROP of 2-*n*-propyl- (*n*PrOx) or 2-*iso*-propyl-2-oxazoline (*i*PrOx) revealed that the apparent polymerization rate per initiating site is independent from the size of the polyfunctional macroinitiator. The LCROP of *n*PrOx or *i*PrOx from macroinitiators follows first-order kinetics and the molar mass of the resulting brush polymers increases linear with the monomer conversion. The molecular brushes with different side chain length show thermal responsive properties, that is, having a defined CP that can be modulated by the side chain length and composition, backbone chain length as well as concentration. Interestingly, the side chain length has a distinct effect on the thermoresponsive solution behavior as for very short pendant chains ($m = 3$), the lyotropic behavior is that of a random coil, while for medium and long side chains ($m \geq 6$), the molecular brush characteristics were found.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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