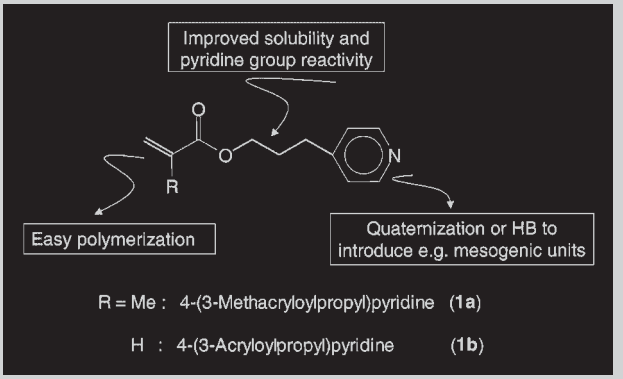
Full Paper: To overcome some drawbacks of polyvinylpyridines, new monomers of acrylate and methacrylate type with pendant pyridine groups i.e., 4-(3-methacryloylpropyl)pyridine **1a** and 4-(3-acryloylpropyl)pyridine **1b** were successfully prepared, although it turned out to be challenging work to synthesize the acrylate monomer **1b**. First polymerization studies showed that the new monomers could be polymerized easily by atom transfer radical polymerization (ATRP). The new polymers show excellent characteristics, such as very good solubility, low glass-transition temperature, and easy quaternization.



Design and structure of new monomers **1a** and **1b**.

Synthesis and Characterization of New Acrylate and Methacrylate Monomers with Pendant Pyridine Groups

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Introduction

Polymers containing pyridine moieties attract much attention. This is mainly because of the presence of the nucleophilic nitrogen atom, which makes possible a variety of reactions, e.g., protonization, quaternization or complexation of metals.[1] In consequence, polyvinylpyridinium salts have found many applications as polyelectrolytes, polysoaps, interpolyelectrolyte complexes with synthetic and natural polyanions, electrically conducting matrices for enzymes, selectively separating membranes, anion exchangers, chemical reagents etc.[2,3] Block and graft copolymers of vinylpyridine monomers are important as thermoplastics, emulsifying agents, and membranes.

In polyvinylpyridines, the pyridine core is directly attached to the main chain, which leads to some characteristic effects, e.g., influence on or steric hindrance of reactions at the pyridine group[1] as well as tacticity in poly(2-vinylpyridine). On the other hand, poly(4-vinylpyridine) has a poor solubility in most solvents, whereas that of poly(2-vinylpyridine) is slightly enhanced.

For those reasons, it would be highly desirable to decouple the functional group, i.e., to separate the pyridine core from the polymer backbone by a spacer, which could influence, among other parameters, chemical structure/properties relationships. For example, spacer segments play a key role in affecting the thermotropic behavior of liquid crystalline polymers.[4]

In general, the polymerization of acrylate and methacrylate monomers, which can be used to prepare structurally well-defined polymers, is well known. This includes living-anionic polymerization,[5] group-transfer polymerization (GTP)[5] and atom transfer radical polymerization (ATRP).[6]

We combined the advantages of acrylate and methacrylate polymerization with those of the spacer-separated pyridine cores by preparing and polymerizing the new monomer 4-(3-methacryloylpropyl)pyridine **1a**, and the corresponding monomer 4-(3-acryloylpropyl)pyridine **1b** (see Scheme 1).

It turned out to be rather challenging to synthesize **1b**, because of a very strong self-quaternization reaction occurring during the conventional synthesis using the acid chloride, which proved successful for the synthesis of the methacrylate monomer **1a**.

In this paper, various attempts to synthesize the monomers and initial proof of their controlled radical polymerizability is described. The polymerization behavior will be presented in more detail in a subsequent paper.

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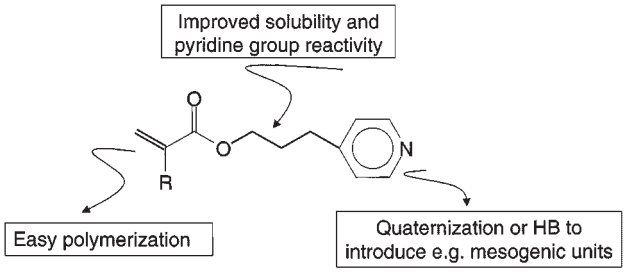


Scheme 1. Design and structure of new monomers **1a** and **1b.**

Experimental Part

Materials

Argon was dried and purified first over molecular sieves (3 Å) and then with potassium dispersed on aluminium oxide. Tetrahydrofuran (THF) and dioxane were distilled over sodium and kept under argon. The other solvents were distilled and kept over molecular sieves. Pyridine, 2,6-dimethylpyridine, and triethylamine were distilled over potassium hydroxide and kept under argon. Commercially available methacryloyl chloride, acryloyl chloride, and 4-(3-hydroxypropyl)pyridine were distilled before use. Methyl acrylate and *tert*-butyl acrylate were distilled with 2,6-di-*tert*-butyl-4-methyl phenol as inhibitor and stored under argon. Tris[2-(dimethylamino)-ethyl]amine (Me_6TREN) was synthesized according to the literature.[7] CuBr was stirred with acetic acid and subsequently washed with ethanol and ether, followed by drying under vacuum. The other chemicals, also obtained commercially, were used without further purification.

Instrumentation

NMR spectra were recorded on a Bruker spectrometer (250 MHz, AC 250). Electron impact mass spectrometry (EI-MS) was recorded with a Varian 312 mass spectrometer. Infrared spectra were recorded with a Digilab FTS-40 FT-IR spectrometer using pellets (ca. 1 mg sample dispersed in 200 mg potassium bromide) or liquid film (sample on potassium bromide plate). Molecular weights and polydispersities were determined by size exclusion chromatography (SEC) at 70 °C using a Waters 150CV+ equipment with the detector RI-WAT 150CV+. Precolumn PSS 50 × 8 mm^2, 5 μm particle size; 2 SDV columns 30 × 8 mm^2, pore width 10^3, 10^5 Å, 5 μm particle size; 150 μl injection volume; approx. 1 mg · ml^{-1} injection concentration. *N*,*N*-dimethylacetamide (DMAc) with added 0.05 M LiCl was used as an eluent with an elution rate of 0.5 ml · min^{-1}. Polystyrene standards were used for column calibration. Alumina was used as stationary phase for thin-layer chromatography (TLC).

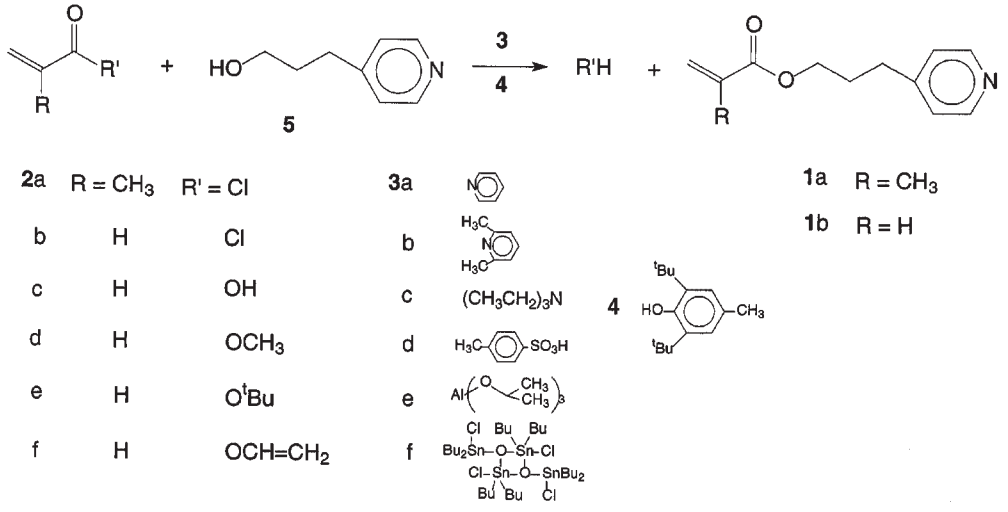
Synthesis

Scheme 2 shows the general synthesis of **1a** and **1b**.

4-(3-Methacryloylpropyl)pyridine **1a**

Methacryloyl chloride **2a** (10.5 g, 0.1 mol) was added dropwise at room temperature over 3 h to a THF solution containing 4-(3-hydroxypropyl)pyridine **5** (13.7 g, 0.1 mol), 7.9 g of pyridine **3a** and 50 mg of 2,6-di-*tert*-butyl-4-methyl phenol **4** as inhibitor. The system was then heated to reflux for a further 5 h. The reaction mixture was poured into 400 ml of an aqueous solution containing 40 g of sodium hydroxide and was subsequently extracted with chloroform (3 × 40 ml). The combined chloroform extracts were dried over night with anhydrous sodium sulfate. The solvent was evaporated under reduced pressure to obtain a brown oil. The product was finally distilled under vacuum with $FeCl_3$ as inhibitor, 83–84 °C at 0.03 mbar, to yield **1a** (15.2 g, 74%). The purity was checked with TLC (cyclohexane/ethyl acetate, 3 : 1).

^{1}H NMR ($CDCl_3$): $\delta = 1.94$ (s, 3H, CH_3), 2.0 (m, 2H, $COOCH_2C\underline{H}_2$), 2.73 (t, 2H, $COOCH_2CH_2C\underline{H}_2$), 4.18 (t, 2H, $COOCH_2$), 5.57 and 6.10 (d, 2H, CH_2=C), 7.16 (d, 2H, *β*-PyH), 8.54 (d, 2H, α-PyH).



Scheme 2. Preparation of monomers **1a** and **1b**.

IR (film on KBr): 2 957, 1 718, 1 637, 1 602, 1 558, 1 497, 1 452, 1 415, 1 320, 1 207, 1 219, 1 165 cm^{-1}.

EI-MS: $m/z = 205$ (M^+, 19%), 118 (100), 92 (24), 69 (24).

4-(3-Acryloylpropyl)pyridine **1b**

Vinyl acrylate **2f** (4.9 g, 0.05 mol), 4-(3-hydroxypropyl)pyridine **5** (6.86 g, 0.05 mol), 1,3-dichloro-1,1,3,3-tetrabutyldistannoxane **3f** (1.1 g, 2 mmol), 2,6-di-*tert*-butyl-4-methyl phenol **4** (0.66 g, 2 mmol), and 10 ml THF were added to a round-bottom flask. The solution was stirred at 50 °C for 48 h. The reaction mixture was separated by column chromatography using aluminium oxide as packing material and a mixture of cyclohexane/ethyl acetate (3 : 1) as eluent. A light yellow liquid (8.2 g, 85%) was obtained. Before polymerization, the monomer was distilled under vacuum with $FeCl_3$ as inhibitor at 85–86 °C at 0.04 mbar.

^{1}H NMR ($CDCl_3$): $\delta = 2.06$ (m, 2H, $COOCH_2C\underline{H}_2$), 2.72 (t, 2H, $COOCH_2CH_2C\underline{H}_2$), 4.19 (t, 2H, $COOC\underline{H}_2$), 5.86 and 6.13 (d and m, 2H, $C\underline{H}_2$=C), 6.36 (d, 1H, CH_2=C$\underline{H}$), 7.14 (d, 2H, β-PyH), 8.50 (d, 2H, α-PyH).

IR (film on KBr): 2 957, 1 724, 1 635, 1 602, 1 559, 1 497, 1 455, 1 409, 1 296, 1 272, 1 191, 1 057 cm^{-1}.

EI-MS: $m/z = 191$ (M^+, 5%), 118 (100), 55 (37), 92 (27), 106 (16).

Synthesis of Poly[4-(3-acryloylpropyl)pyridinium] **6**

Acryloyl chloride **2b** (2.08 g, 0.02 mol) was added dropwise to a THF solution containing 4-(3-hydroxproply)pyridine **5** (2.74 g, 0.02 mol) over 1 h. The mixture was then stirred for 5 h at room temperature. A yellow viscous solid was precipitated. The viscous solid was dissolved in water, precipitated from acetone and dried under vacuum at room temperature. A yellow solid (4.5 g, 93%) was obtained.

IR (KBr pellet): 3 398, 3 051, 2 597, 2 049, 1 986, 1 721, 1 640, 1 571, 1 517, 1 471, 1 401, 1 174, 1 053 cm^{-1}.

A ^{1}H NMR spectrum was recorded in D_2O (with the sodium salt of 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid as internal standard), as shown in Figure 1 (see *Results and Discussion*).

Polymerization

Poly[4-(3-methacryloylpropyl)pyridine] **P-1a**

A round-bottom flask with a stirring bar was charged with copper bromide (8.6 mg, 0.06 mmol), Me_6TREN (14 mg, 0.06 mmol), **1a** (2.05 g, 10 mmol), and ethyl 2-bromoisobutyrate (23 mg, 0.12 mmol). Three freeze-pump-thaw cycles were performed and the flask was sealed under vacuum. The flask was then put in a water bath at 25 °C. The system quickly become more viscous. The reaction system was kept at 25 °C for a further 3 h. Afterwards, the content was dissolved in chloroform and passed through an alumina column to remove the metal containing residues. After evaporation of the solvent, the residue was dissolved in a small amount of chloroform and precipitated in cold ether. A solid was obtained and dried at 50 °C under vacuum.

^{1}H NMR ($CDCl_3$): $\delta = 0.87$–1.24 (3H, CH_3 in main chain), 1.93 (4H, CH_2 in main chain and $COOCH_2C\underline{H}_2$), 2.65 (2H, $COOCH_2CH_2C\underline{H}_2$), 3.95 (2H, $COOC\underline{H}_2$), 7.1 (2H, β-PyH), 8.47 (2H, α-PyH).

Poly[4-(3-acryloylpropyl)pyridine] **P-1b**

ATRP of **1b** with copper bromide (7.2 mg, 0.05 mmol), Me_6TREN (11.5 mg, 0.05 mmol), **1b** (1.15 g, 6 mmol), and ethyl 2-bromoisobutyrate (19.5 mg, 0.1 mmol) was carried out in the similar manner as for **1a** and the polymer was finally obtained as a viscous liquid.

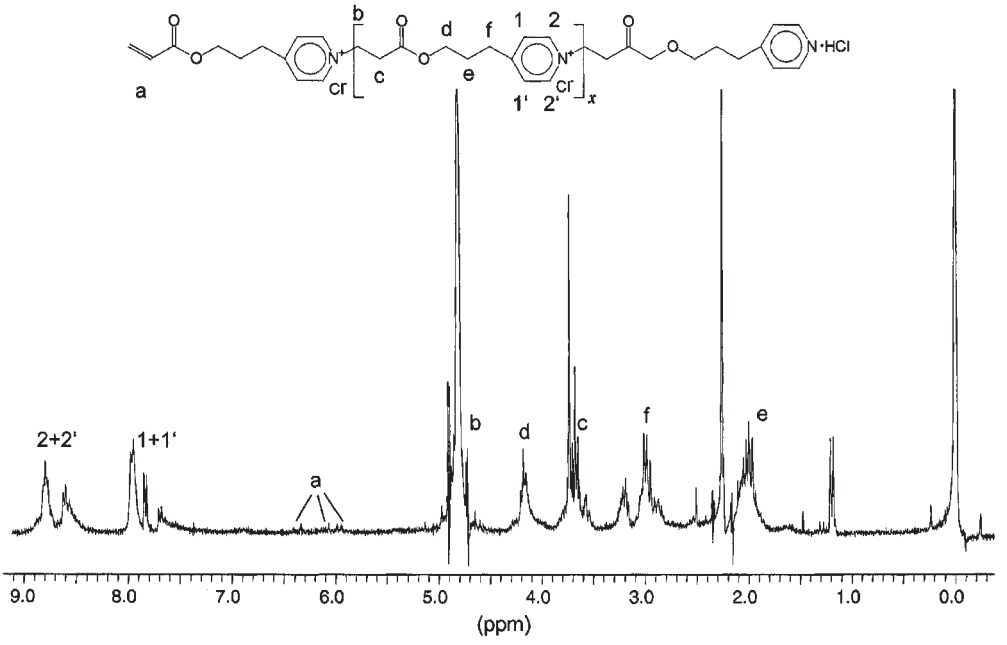


Figure 1. ^{1}H NMR spectrum of poly[4-(3-acryloylpropyl)pyridinium] **6** (in D_2O).

Table 1. Synthesis of methacrylate monomer **1a** and acrylate monomer **1b**.

Entry	**2**	**5**	**3**	**4**	Conditions	Yield **1**[a]
	mol	mol	mol	mol		%
1	**2a** (0.15)	0.15	**3a** (0.1)	0.001	THF, 0–5 °C (1 h), RT (5 h)	**1a**, 74
2	**2b** (0.115)	0.1	**3a** (0.2)	0.002	THF, 0–5 °C (1 h), RT (5 h)	**1b**, < 5[b]
3	**2b** (0.15)	0.15	**3a** (1.5)	0.003	–[c], 0–5 °C (1 h), RT (5 h)	**1b**, < 5[b]
4	**2b** (0.15)	0.15	**3b** (0.15)	0.003	THF, 0–5 °C (1 h), RT (5 h)	**1b**, < 5[b]
5	**2b** (0.15)	0.15	**3c** (0.2)	0.002	THF, 0–5 °C (1 h), RT (5 h)	**1b**, < 10[b]
6	**2b** (0.2)	0.05	**3c** (0.1)	0.003	Dioxane, 0–5 °C (1 h), RT (5 h)	**1b**, < 5[b]
7	**2c** (0.075)	0.05	**3d** (0.005)	0.005	Chloroform, reflux, 20 h	**1b**,–[d]
8	**2d** (0.05)	0.05	**3e** (0.005)	0.0025	Hexane, reflux, 24 h	**1b**,–[e]
9	**2d** (0.14)	0.05	**3f** (0.005)[f]	0.005	–[c], 45 °C, 72 h	**1b**, 17.3
10	**2e** (0.25)	0.1	**3f** (0.002)[f]	0.002	–[c], 50 °C, 96 h	**1b**,–[e]
11	**2f** (0.05)	0.05	**3f** (0.001)[f]	0.002	THF, 50 °C, 96 h	**1b**, 31.4
12	**2f** (0.1)	0.15	**3f** (0.002)[f]	0.002	–[c], 50 °C, 72 h	**1b**, 36.6
13	**2f** (0.05)	0.05	**3f** (0.002)[f]	0.003	THF, 50 °C, 48 h	**1b**, 85

[a] Isolated yield after column chromatography.
[b] Determined by ^{1}H-NMR spectroscopy.
[c] Pyridine, methyl acrylate, *tert*-butyl acrylate or 4-(3-hydroxypropyl)pyridine were used as solvent.
[d] No water was separated off by a water separator.
[e] No product was detected by TLC.
[f] Molarity on the basis of the monomeric formulation.

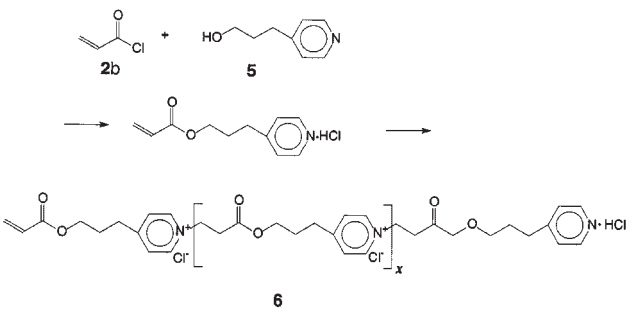
^{1}H NMR ($CDCl_3$): $\delta = 1.3–1.9$ (4H, CH_2 in main chain and $COOCH_2C\underline{H}_2$), 2.31 (1H, CH in main chain), 2.56 (2H, $COOCH_2CH_2C\underline{H}_2$), 3.98 (2H, $COOC\underline{H}_2$), 7.05 (2H, β-PyH), 8.46 (2H, α-PyH).

Results and Discussion

According to Scheme 2 and as shown in entry 1 of Table 1, **1a** can be easily prepared by a general esterification method with a yield of 74% by reacting methacryloyl chloride **2a** with 4-(3-hydroxypropyl)pyridine **5** in the presence of pyridine **3a**, which acts as base to absorb the hydrogen chloride released upon reaction. A similar method, starting with acryloyl chloride **2b**, is not successful for preparing **1b**. Different bases including pyridine **3a**, 2,6-dimethylpyridine **3b**, and triethylamine **3c** were used. In addition, the solvent was changed from THF to dioxane, and even to pyridine.[8] In all cases, the yield is very low (entry 2–6 in Table 1). An alternate attempt of an esterification using acrylic acid **2c** with 4-(3-hydroxypropyl)pyridine **5** and using **3d** as catalyst was carried out. No water was separated, which indicated that no esterification reaction took place (entry 7 of Table 1).

The above results led us to the conclusion that a strong side reaction took place. We assumed that the pyridine moiety of **5** was protonated in-situ during the course of the reaction and that the protonated pyridinium moiety subsequently reacted directly with the double bond to produce a self-quaternized water-soluble ionic polymer. A report of a similar reaction was described for 4-vinylpyridine, which, after protonation by monomeric or polymeric acids, polymerizes spontaneously via the pyridine ring to give the corresponding quaternized poly(4-vinylpyridinium) salt.[9] Furthermore, Chapman et al.[10] reported that pyridinium salts can be obtained by a reaction of protonated heterocycles with methyl vinyl ketone.

As a ''side-product'', poly[4-(3-acryloylpropyl)pyridinium] **6** was prepared intentionally to confirm the proposed side reaction mechanism (see Scheme 3). The proton NMR spectrum of poly[4-(3-acryloylpropyl)pyridinium] **6** was recorded in D_2O. As shown in Figure 1, the peaks from the protons attached on the double bond are much decreased and a new signal from the methylene attached to the nitrogen of the pyridine ring has appeared. The signal from the proton attached to a quaternized pyridine ring was also shifted to lower field. These results led to confirmation of the proposed 'side reaction' mechanism.



Scheme 3. Synthesis of poly[4-(3-acryloylpropyl)pyridinium] **6** (proof of the synthetic 'side reaction' of **1b**).

Table 2. Reaction conditions and molecular weights of **P-1a** and **P-1b**.

Polymer	Reaction condition					Conversion[b]	Molecular weight		
	Monomer	Initiator[a]	CuBr	Me_6TREN	Time	%	$\overline{M}_{n,th}$	$\overline{M}_{n,th}$	$\overline{M}_w/\overline{M}_n$
	mmol	mmol	mmol	mmol	h		10^4	10^4	
P-1a	10	0.12	0.06	0.06	3	80	1.367	1.58	1.21
P-1b	6	0.1	0.05	0.05	8	61	0.699	1.12	1.07

[a] Ethyl 2-bromoisobutyrate.
[b] Determined by ^{1}H NMR spectroscopy.

Thus in order to synthesize the designed pyridine monomer of acrylate type **1b** it is crucial to avoid protonation of the pyridine moiety. Therefore, no acidic reactants can be used. A transesterification of 'neutral' methyl acrylate **2d** with 4-(3-hydroxypropyl)pyridine using **3d** as catalyst was carried out. However, the acidic catalyst prevented product formation (entry 7 of Table 1). After further attempts, we used as neutral catalyst 1,3-dichloro-1,1,3,3-tetrabutyldistannoxane **3f**, reported by Otita et al.[11] As shown in entry 9 of Table 1, a transesterification of methyl acrylate **2d** only gave a yield of 17.3% due to the slow rate and reversibility of the reaction. In another attempt using *tert*-butyl acrylate **2e**, no product was detected by TLC, perhaps because of the steric hindrance of the catalytic activity of **3f**. In order to get a high yield, vinyl acrylate **2f** was finally used as a reactant in an analogy to the literature.[11] The reaction could eventually reach high conversion, because the produced vinyl alcohol was capable of escaping from the equilibrium system by its conversion into acetaldehyde. It was found that when vinyl acrylate **2f** was used, the easily occurring polymerization of both **2f** and the formed acrylate monomer **1b** further decreased the yield. As shown in entry 11, Table 1, a yield of 31.4% was obtained. Even when a large amount of 4-(3-hydroxypropyl)pyridine **5** was used, the yield was not much improved (entry 12). The polymerization was avoided by using a higher concentration of inhibitor **4** and reacting for a shorter time. The latter required a high concentration of catalyst **3f**. Finally, as shown in entry 13, Table 1, a high yield of 85% was successfully obtained.

Polymerization of pyridine containing monomers is a challenging problem for ATRP because these monomers and corresponding polymers are, in principle, strong coordinating agents themselves, which can compete with the complexing agent for the binding of the metal catalysts in those systems. Therefore, a strong complexing agent should be used. ATRP of 4-vinylpyridine was performed by Matyjaszewski et al. using Me_6TREN as a strong ligand to decrease the competition of the pyridine group.[12] Likewise, bulk ATRP of the new monomers was carried out here using ethyl 2-bromoisobutyrate as initiator and CuBr complexed by Me_6TREN as catalyst at 25 °C. Both new monomers can be easily polymerized with such an initiator/catalyst system. The data of the reaction conditions are summarized in Table 2.

The reaction systems quickly became viscous and for **1a**, finally becoming a green solid. The color (metal containing residues) could be removed by passing a chloroform solution of the crude polymer over a small alumina column. Both polymers show very good solubility in normal solvents, such as THF, acetone and chloroform.

SEC curves of the polymers are shown in Figure 2. We used DMAc with added 0.05 M LiCl as an eluent system, but not because of a bad solubility of the polymers in THF. Here, an interaction of the highly polar polymers with the polystyrene matrix (appearance of a pronounced peak tailing) and a strong association behavior of the polymers (shift to higher molecular weights and broadening of the peaks) occurs. To reduce or avoid these phenomena, it was necessary to use the highly polar eluent system described above. The polymer obtained from **1a** (**P-1a**) exhibits a $\overline{M}_{n,SEC} = 1.58 \times 10^4$ with a dispersity of $\overline{M}_w/\overline{M}_n = 1.21$, and that from **1b** (**P-1b**) exhibits a $\overline{M}_{n,SEC} = 1.12 \times 10^4$ with

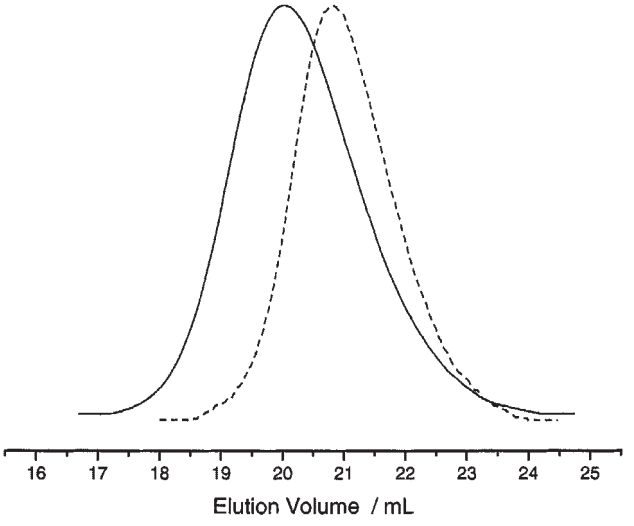


Figure 2. SEC curves of poly[4-(3-methacryloylpropyl)pyridine] **P-1a** (solid line) and poly[4-(3-acryloylpropyl)pyridine] **P-1b** (dotted line).

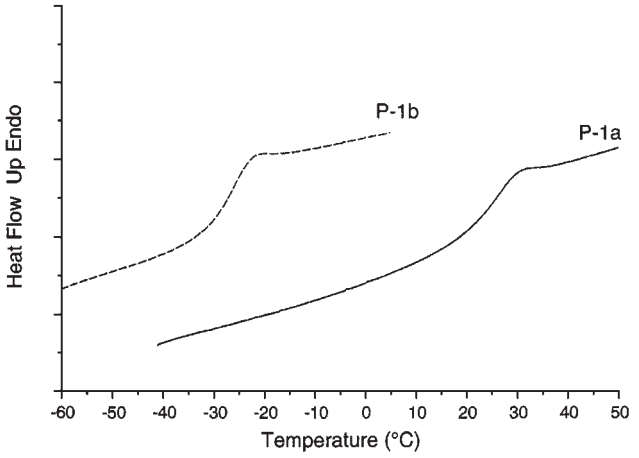


Figure 3. DSC curves of **P-1a** and **P-1b**, heating rate $10\ \mathrm{K \cdot min^{-1}}$.

$\overline{M}_w/\overline{M}_n = 1.07$ (see Table 2). Further investigations of the polymerization will be described in more detail in a subsequent publication.

DSC measurements (see Figure 3) only exhibit glass transitions for **P-1a** around room temperature and for **P-1b** at -27 °C. These low values are because of the flexible acrylate/methacrylate main chain and the propyl spacer.

Conclusion

New monomers i.e., 4-(3-methacryloylpropyl)pyridine and 4-(3-acryloylpropyl)pyridine with spacer linked pyridine groups, were successfully prepared. As a side reaction, the formation of new poly[4-(3-acryloylpropyl)pyridinium] was achieved. The new polymers, poly[4-(3-methacryloylpropyl)pyridine] and poly[4-(3-acryloylpropyl)pyridine] obtained by ATRP showed very good solubility in normal solvents, and a low glass-transition temperature. The polymers offer excellent opportunities for the introduction of functional groups e.g., via quaternization or hydrogen bonding.

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