Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Liquid Crystalline Poly[(N-3,4-*Bis*(Decyloxy)Benzoyl)-Ethyleneimine] *Via* Cationic Polymerization

U. Stebani[a]; G. Lattermann[a]
[a] Makromolekulare Chemie I, Universität Bayreuth, Bayreuth, Germany

To cite this Article Stebani, U. and Lattermann, G.(1995) 'Liquid Crystalline Poly[(N-3,4-*Bis*(Decyloxy)Benzoyl)-Ethyleneimine] *Via* Cationic Polymerization', Journal of Macromolecular Science, Part A, 32: 1, 385 — 401
To link to this Article: DOI: 10.1080/10601329508019184
URL: http://dx.doi.org/10.1080/10601329508019184

MACROMOLECULAR REPORTS, A32(SUPPL. 3), 385-401 (1995)

LIQUID CRYSTALLINE POLY[(N-3,4-*BIS*(DECYLOXY)BENZOYL)-ETHYLENEIMINE] *VIA* CATIONIC POLYMERIZATION

U. STEBANI, G. LATTERMANN*

Makromolekulare Chemie I, Universität Bayreuth
D-95440 Bayreuth, Germany

ABSTRACT

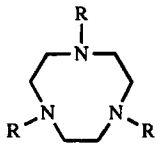
We describe for the first time the synthesis of liquid crystalline side chain polymers with a linear poly(ethyleneimine) (LPEI) backbone via cationic polymerization. Thus, the mesogenic Poly[(N-3,4-bis(decyloxy)benzoyl)ethyleneimine] was prepared from the corresponding, non mesogenic 2-oxazoline monomer. The narrow weight distribution indicates the living character. Furthermore, the same method was used for the synthesis of a liquid crystalline macromonomer with a terminal double bond. Surprisingly some of the low-molecular intermediates also exhibit mesogenic behaviour. Their thermal properties are likewise described.

1. INTRODUCTION

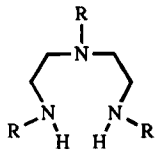
At the beginning of our work on mesogenic properties of different amides with 'two chain' substituents, we investigated liquid crystalline azacyclic derivatives of hexacyclene, 1,4,8,11-tetraazacyclotetradecane, cyclam, 1,5,9-triazacyclododecane, and 1,4,7-triazacyclononane, all exhibiting 3,4-bis(alkoxy)benzoyl substitutents [1,2]. Especially with the triazacyclononane derivatives **1** we

performed further investigations. Thus, the reduction of the amide groups to amines leads to a higher flexibility of the ring and results in a complete loss of liquid crystallinity [3]. Subsequently, mesomorphism can be reinduced by protonating the amine groups [4], which increases the interactions between the single molecules through strong coulombic forces, as it is known from other low molecular ammonium mesogens [5]. Another possibility of inducing mesomorphism through an increased stiffness of the central azacyclic amine core is the complexation with transition metals. This was proved by the synthesis of different metallomesogens with a substituted triazacyclononane ligand [3,6].

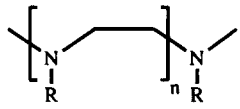
In the course of these investigations the question arose, how the "opening" of the central ring of azacyclic amides, which leads to a linear amide backbone, would influence the mesogenic behaviour. We found, that the 3,4-bis(alkoxy)benzoyl substituted "open chain" analogues of the triazacyclononane derivatives **1**, i.e. diethylenetriamine derivatives **2**, still exhibits monotropic mesomorphism with the additional appearance of apparently cubic phases [7]. The elongation of the linear backbone, which leads for example to triethylenetetramine derivatives, as well as the elongation of the ethylene to propylene bridges between the amide groups, causes a remarkable stabilisation of the liquid crystalline phase [8].



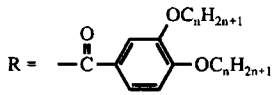
1



2



3



We wanted to know, if in consequence even the corresponding polymer with 'two chain' substituents, i.e. the 3,4-bis(alkoxy)benzoyl substituted linear poly(ethyleneimine) (LPEI) **3**, still exhibits liquid crystalline properties.

Till now, two liquid crystalline side chain polymers with a linear poly(ethyleneimine) backbone are known. All have been obtained by a polymer-analogous alkylation of the unsubstituted polymer. To induce mesomorphism two

principles were used so far: attaching of a classical mesogenic unit in the side group [9] and/or quaternisation of the tertiary amino groups to the main chain [9,10]. The ammonium group containing polymers are further examples for the above mentioned ability of coulombic forces to induce liquid crystallinity.

Our intention was to synthesize the 3,4-bis(alkoxy)benzoyl substituted poly(ethyleneimine) **3** through cationic polymerization of the corresponding 2-oxazoline monomer. In principle this method exhibits living character for medium molecular weights [11] and avoids an incomplete substitution of the imino units in the LPEI backbone, which can be intrinsically a problem of the corresponding polymeranalogous reaction [10].

2. EXPERIMENTAL

2.1. METHODS

FTIR: BioRad Digilab FTS-40. ^{1}H-NMR: Bruker AC 250 (250 MHz). ^{13}C-NMR: Bruker AC 250 (62,5 MHz). MS: Varian 312. Size Exclusion Chromatography (SEC): Waters ALC 200; RI-detector Melz LCD 201; UV-detector Waters 440, 254 nm; eluent THF, elution rate 0.5 mL/min; 2x60 cm PL columns, 5 µm particle size, 100 and 500 Å pore width. Polarisation microscopy: Leitz Labolux 12-Pol, Mettler hot stage FP 82, photo-automat Wild MPS 45/51 S. Thermal analysis: Perkin Elmer DSC 7. Elemental analysis: Mikroanalytisches Labor Ilse Beetz, Kronach.

2.2. MATERIALS

All starting materials were commercially available in high purity and used without further purification. 1,2-Dichlorobenzene was stirred over P_2O_5 over night and distilled over P_2O_5 under inert gas. Argon was first dried over molecular sieve 4Å and then over potassium on neutral aluminium oxide (Alox N). The monomer was freeze dried from benzene solution over night before use. All polymerization reactions were performed under inert gas atmosphere. The synthesis of compound **4** has been described elsewhere [12].

Intermediates and monomer:

N-(3,4-bis(decyloxy)benzoyl)-2-aminoethanol **5**:

10 0 g (21.7 mmol) of the 3,4-bis-(decyloxy)benzoic acid ethylester were dissolved in 100 ml (101.5 g, 1.66 mol) of ethanolamine and refluxed for 5 hours. After that time, the volume of the mixture was reduced under vacuum to a half. The remaining oily liquid was diluted with 400 ml ethanol. After cooling in a refrigerator for 12 h, the crude product precipitated and was filtered off. The subsequent recrystallization twice from ethanol yielded 7.92 g (76%) of the pure product.

IR (KBr, cm^{-1}): 3400, 3285, 2922, 2852, 1633, 1602, 1582, 1544, 1513, 1468, 1393, 1274, 1226, 1136, 762, 721. ^{1}H-NMR ($CDCl_3$, ppm): 7.4 (d, 1H, aromatic), 7.25 (dd, 1H, aromatic), 6.8 (d, 1H, aromatic), 6.65 (s, br, 1H, -N*H*-), 4.0 (t, 4H, -O-CH_2-), 3.8 (t, 2H, -CH_2-OH), 3.55 (m, 2H, -NH-CH_2-), 2.7-3.0 (br, 1H, -O*H*), 1.8 (m, 4H, -O-CH$_2$-CH_2-), 1.1-1.6 (m, 28H, alkoxy -CH_2-), 0.85 (t, 6H, -CH_3). ^{13}C-NMR ($CDCl_3$, ppm): 166.4 (-N-*C*O-), 152.0, 148.8, 126.4, 119.8, 112.7, 112.2 (aromatic), 69.3, 69.0 (-O-*C*H$_2$-), 62.1 (-*C*H$_2$-OH), 42.7 (-NH-*C*H$_2$-), 31.6-22.6 (alkoxy), 14.0 (-*C*H$_3$). MS (m/e): 477 (M$^{\cdot+}$, 33%), 179 (100%). Elemental analysis: Calc. for $C_{29}H_{51}NO_4$: C 72.91, H 10.76, N 2.93 O 13.40; Found: C 72.93, H 10.73, N 2.97, O 13.37 (diff. to 100%).

N-(3,4-bis(decyloxy)benzoyl)-1-amino, 2-chloroethane **6**:

5.0 g (10.5 mmol) of **5** were dissolved in 50 ml thionylchloride and refluxed for 3 hours. After gas development has seized, the remaining $SOCl_2$ was completely evaporated under reduced pressure. Then, the residue was recrystallized three times from ethylacetate to give 3.51 g (67 %) of the pure product.

Differences to **5**: IR (KBr, cm^{-1}): 3265, 1637. ^{1}H-NMR ($CDCl_3$, ppm): 4.0 (m, 4H, -O-CH_2-), 3.65-3.85 (m, 4H, -NH-CH_2-CH_2-Cl). ^{13}C-NMR ($CDCl_3$, ppm): 44.1 (-*C*H$_2$-Cl), 41.7 (-NH-*C*H$_2$-). MS (m/e): 496 (M$^{\cdot+}$, 2%), 179 (100%). Elemental analysis: Calc. for $C_{29}H_{50}ClNO_3$: C 70.20, H 10.16, N 2.82, Cl 7.15, O 9.67; Found: C 70.30, H 10.21, N 2.88, Cl 7.30, O 9.31 (diff. to 100%).

2-(3,4-bis(decyloxy)phenyl)-2-oxazoline **7**:

1.75 g (3.53 mmol) of **6** and 0.60 g (10.6 mmol) KOH were dissolved in ethanol and stirred at 50°C. After 1 hour the cyclization reaction, controlled by TLC, was

completed. The ethanol was evaporated under reduced pressure, the residue redissolved in chloroform and extracted twice with water. The organic layer was dried over sodium sulfate and the solvent evaporated again. Purification of the resulting solid was performed by column chromatography on silica gel, eluent hexane:ethylacetate (volume ratio = 1:1). Yield: 1.46 g (90%).

Differences to **5**: IR (KBr, cm^{-1}): 1652, 1361, 963, 705. ^{1}H-NMR ($CDCl_3$, ppm): 7.4-7.5 (m, 2H, aromatic), 6.8 (d, 1H, aromatic), 4.4 (t, 2H, =N-CH_2-), 4.0 (m, 6H, -O-CH_2-). ^{13}C-NMR ($CDCl_3$, ppm): 164.5 (-N=*C*-O-), 67.4 (=C-O-*C*H_2-), 54.8 (=N-*C*H_2-). MS (m/e): 459 ($M^{\cdot+}$, 65%), 179 (100%). Elemental analysis: Calc. for $C_{29}H_{49}NO_3$: C 75.77, H 10.74, N 3.05, O 10.44; Found C 75.88, H 10.67, N 3.16, O 10.29 (diff. to 100%).

N-Methyl-2-(3,4-bis(decyloxy)phenyl)-2-oxazolinium trifluoromethanesulfonate **8**: 1.32 g (2.87 mmol) of **7** were dissolved in 20 ml of dry diethylether under inert gas atmosphere and slowly added to an ice cooled solution of 0.57 g (0.39 ml, 3.45 mmol) methyl trifluoromethanesulfonate in 10 ml diethylether. A white solid precipitated immediatly. After adding further 30 ml of diethylether the mixture was stirred for 2 hours at room temperature. Then the precipitation was completed over night in a refrigerator. The product was filtered off under inert gas atmosphere, washed with cooled diethylether and dried in vacuo. Yield: 1.38 g (77%).

IR (KBr, cm^{-1}): 2955, 2918, 2849, 1637, 1596, 1468, 1458, 1264, 1151, 1031, 717. ^{1}H-NMR ($CDCl_3$, ppm): 7.55 (dd, 1H, aromatic), 7.35 (d, 1H, aromatic), 7.25 (d, 1H, aromatic), 5.0 (t, 2H, =N^+-CH_2-), 4.3 (t, 2H, -O^+-*C*H_2-), 4.1 (t, 2H,-O-CH_2-), 4.0 (t, 2H, -O-CH_2-), 3.5 (s, 3H, =N^+-CH_3), 1.65-1.85 (m, 4H, -O-CH_2-*C*H_2-), 1.1-1.5 (m, 28H, alkoxy -CH_2-), 0.85 (t, 6H, -CH_3). ^{13}C-NMR ($CDCl_3$, ppm): 170.0 (-N=*C*$^+$-O-), 155.4, 149.2, 125.1, 114.1, 112.3, 111.0 (aromatic), 120.5 (q, -*C*F_3, $^1J_{C-F}$ = 318 Hz), 70.3 (-O^+-*C*H_2-), 69.5, 69.3 (-O-*C*H_2-), 36.3 (=N^+-*C*H_3), 22.6-31.8 (alkoxy), 14.0 (-*C*H_3). Elemental analysis: Calc. for $C_{31}H_{52}F_3NO_6S$: C 59.69, H 8.40, N 2.25, O 15.39, S 5.14, F 9.14; Found C 59.64, H 8.36, N 2.38, O 15.38, S 5.11, F 9.13 (diff. to 100%).

N-(4-vinylbenzyl)piperazine [11]:

21.3 g (0.25 mol) of dry piperazine were dissolved in dry chloroform. 2.52 g (16.5 mmol) of 4-vinylbenzylchloride were slowly added under ice-cooling. After

complete addition, the solution was stirred at room temperature for 10 hours. Then the precipitated piperazinium hydrochloride was filtered off and the filtrate was washed five times with 200 ml portions of water, until the washings were neutral. The organic layer was dried over sodium sulfate and the solvent evaporated. The oily residue was freeze dried from benzene solution. Yield: 3.01 g (91%).
IR (KBr, cm^{-1}): 3414, 3085-3000, 2938, 2809, 1630, 1512, 1458, 1109, 908, 730. ^{1}H-NMR ($CDCl_3$, ppm): 7.3 (m, 4H, aromatic), 6.7 (d, 1H, ar-C*H*=), 5.7 (d, 1H, =CH_2), 5.2 (d, 1H, =CH_2), 3.45 (s, 2H, -CH_2-), 2.9 (m, 4H, HN-CH_2-), 2.4 (m, 4H, -CH_2-N), 1.5 (s, 1H, -N-*H*). ^{13}C-NMR ($CDCl_3$, ppm): 137.8, 136.1, 129.1, 125.8 (aromatic), 136.4 (=*C*H-), 113.2 (=CH_2), 63.1 (ar-CH_2-N), 54.2, 45.8 (-N-CH_2-CH_2-N-).

Polymers:

General synthesis:
To a solution of the freshly freeze dried monomer **7** in dry o-dichlorobenzene the methyl trifluoromethanesulfonate was added under inert gas atmosphere. The mixture was stirred for six days at 70°C. For termination, the corresponding amine was added and the solution was stirred for another hour at room temperature. Then the reaction mixture was diluted with chloroform to twice the volume and extracted two times with water. The organic layer was dried over sodium sulfate and the chloroform evaporated under reduced pressure. The remaining amounts of o-dichlorobenzene and of some by-products were separated by column chromatography (silica gel): the crude product was redissolved in hexane:ethylacetate (volume ratio = 1:1) and chromatographed with the same mixture as eluent until all by-products were washed out off the column. The pure product was then extracted from the column either with chloroform (polymer **9**) or with ethylacetate:methanol (volume ratio = 1:1) as eluent (polymer **10**). Then, the solvents were evaporated under reduced pressure and the oily residues were freeze dried from benzene solution.

α-Methyl-ω-piperidinyl-poly(N-(3,4-bis(decyloxy)benzoyl)ethyleneimine) **9**:
2.01 g (4.40 mmol) monomer **7**; 58.7 mg (0.36 mmol) methyl trifluoromethanesulfonate; 10 ml o-dichlorobenzene; 0.10 ml (86.5 mg, 1.0 mmol) piperidine. Yield: 1.32 g (64%).

IR (KBr, cm^{-1}): 2924, 2855, 1631, 1602, 1582, 1516, 1467, 1430, 1267, 1139, 1015, 759. ^{1}H-NMR ($CDCl_3$, ppm): 6.5-6.9 (m, br, aromatic), 3.8-4.1 (m, br,-O-CH_2-), 2.0-3.7 (m, br, -N-CH_3, -N-CH_2-CH_2-N-, -N-CH_2-), 1.65-1.85 (m, br, -O-CH_2-CH_2-, piperidinyl-CH_2-), 1.1-1.5 (m, br, alkoxy -CH_2-), 0.85 (t, -CH_3). ^{13}C-NMR ($CDCl_3$, ppm): 171.8 (-C=O), 149.6, 148.6, 127.9, 119.7, 112.7, 112.0 (aromatic), 69.1, 68.8 (-O-CH_2-), 54.7 (-N-CH_3), 45.7, 39.7 (br, -N-CH_2-CH_2-), 22.7-31.9 (alkoxy), 24.2 (γ-CH_2-piperidinyl), 14.0 (-CH_3).

α-Methyl-ω-(4-vinylbenzylpiperazinyl)-poly(N-(3,4-bis(decyloxy)benzoyl)ethylene-imine) **10**:

2.60 g (5.66 mmol) monomer **7**; 92.5 mg (0.56 mmol) methyl trifluoromethanesulfonate; 20 ml o-dichlorobenzene; 0.23 g (1.2 mmol) N-(4-vinylbenzyl)piperazine. Yield: 2.01 g (73%).

IR (KBr, cm^{-1}): 2924, 2855, 1631, 1602, 1582, 1516, 1467, 1430, 1267, 1139, 1015, 759. ^{1}H-NMR ($CDCl_3$, ppm): 6.5-7.0 (m, br, aromatic), 5.7, 5.2 (m, br, -CH=CH_2), 3.8-4.1 (m, br,-O-CH_2-), 2.0-3.7 (m, br, -N-CH_3, -N-CH_2-CH_2-N-, -N-CH_2-), 1.65-1.85 (m, br, -O-CH_2-CH_2-, γ-CH_2-piperidinyl), 1.1-1.5 (m, br, alkoxy -CH_2-), 0.85 (t, -CH_3). ^{13}C-NMR ($CDCl_3$, ppm): 172.0 (-C=O), 150.1, 148.9, 128.0, 119.6, 112.7, 111.6 (aromatic), 136.2 (-CH=), 126.3 (=CH_2), 69.1, (-O-CH_2-), 52.2 (-N-CH_3), 47.5, 39.7 (br, -N-CH_2-CH_2-), 22.6-31.7 (alkoxy), 14.0 (-CH_3).

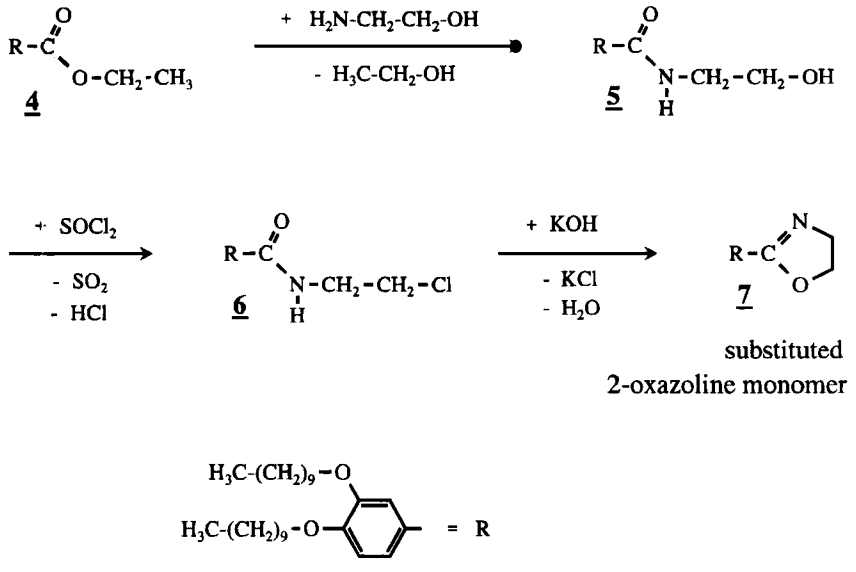
3. RESULTS AND DISCUSSION

3.1. SYNTHESIS

The synthesis of the monomer (scheme 1) was carried out according to the literature [13]. Because of an unsuccessful direct cyclization of the ethanolamide **5** with $SOCl_2$, a further reaction step had to be added, according to reference [14].

The polymerization of **7** (Scheme 2) was carried out in analogy to Saegusa's method for 2-aryl-2-oxazolines [13], which was improved recently by Nuyken et al. [11].

When diethylether was used as solvent at room temperature, the initiating oxazolinium species **8**, which is obtained by adding methyl trifluoromethane-



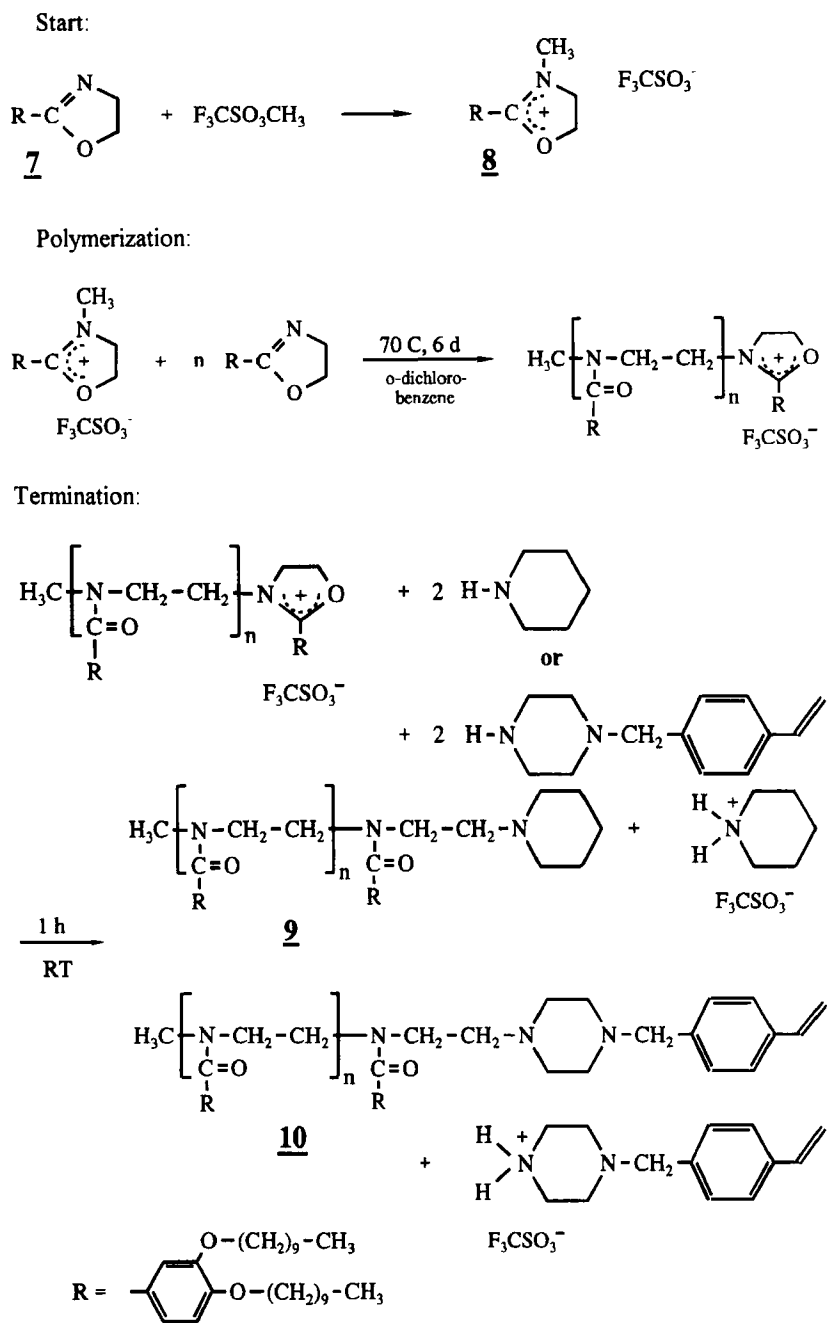
SCHEME 1. Synthesis of 2-(3,4-bis(decyloxy)phenyl)-2-oxazoline

sulfonate to the 2-oxazoline monomer 7, can be isolated and characterized. In the presence of o-dichlorobenzene as solvent and further monomer 7 the polymerization reaction proceeds slowly at elevated temperatures. Because of our bulky 'two chain' substituents, we have performed the polymerization reaction during six days at 70°C.

The termination of the polymerization reaction was achieved according to the systematic investigations of Nuyken et al. [11], who showed that cycloaliphatic amines are very efficient termination agents and N-(4-vinylbenzyl)piperazine is most suitable for the synthesis of macromonomers of e.g. poly[(N-benzyl)-ethyleneimine]. This method was succesfully applied to the conversion of 7 into the corresponding macromonomer **10**.

The molar masses of the polymers were determined by size exclusion chromatography (SEC). As an example, the chromatogram of **9** is given in Figure 1.

All polymerization data are shown in Table 1.



SCHEME 2. Polymerization of the substituted 2-oxazoline monomer

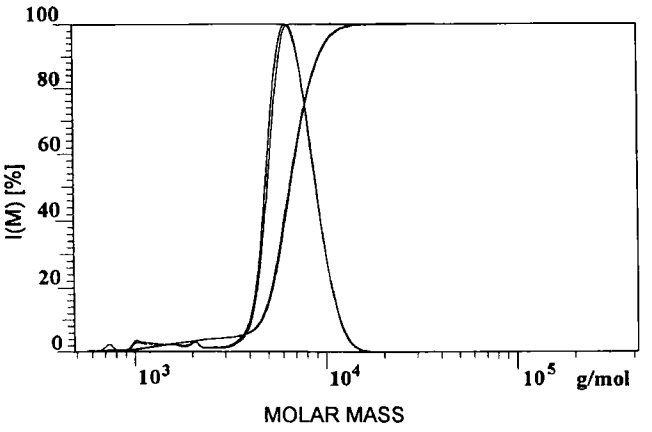


FIGURE 1. SEC chromatogram of polymer **9**.

TABLE 1. Polymerization data of compounds **9** and **10**. [M]: monomer concentration, [I]: starter concentration of methyl trifluoromethanesulfonate; polystyrene standard used for SEC calibration.

compound	$\frac{[M]}{[I]}$	$M_{calc.}$	$\overline{M_w}$	$\overline{M_n}$	$\frac{\overline{M_w}}{\overline{M_n}}$
9	12:1	5617	6740	5590	1.20
10	10:1	4814	3040	2800	1.08

In case of polymer **9**, the values of the molar mass $M_{calc.}$, calculated from the initial monomer/initiator ratio [M]/[I] for a conversion of 100%, and the experimental values for the weight average molar mass $\overline{M_w}$ resp. the number average molar mass $\overline{M_n}$, fit quite well, although a polystyrene standard was used for SEC calibration. A 100% conversion during the polymerization reaction was assumed because no unreacted monomer **7** was isolated during the purification procedure. Apparently, the obtained yield of **9** is mainly related to the working up loss caused by the column chromatography. For polymer **10**, the experimental data

reveal a lower mass than the calculated value. This should be explained by the fact, that the chosen concentration of the active species in o-dichlorobenzene was only the half with respect to the polymerization procedure of **9** (see experimental part). Apparently the resulting lower polymerization rate is responsible for the incomplete monomer conversion during the rather very slow polymerization reaction (6 days). In fact, contrary to the synthesis of **9**, a certain amount of unreacted monomer **7** could be isolated during the purification procedure of the macromonomer **10**.

Both polymers show a monomodal and narrow molecular weight distribution (cf. Figure 1). At least in the case of the macromonomer **10**, the living character of this polymerization procedure is indicated by the low polydispersity index of 1.08.

The functionality of macromonomer **10** with respect to the terminal double bond was determined by ^{1}H-NMR-measurements. For this the relation of the integrals of the vinyl protons and the rather well separated methyl groups of the alkoxy chain were evaluated. The calculated functionality of 1.05 can be considered as ideal, if the accuracy of this method is taken into account.

3.2. THERMAL BEHAVIOUR

Surprisingly two intermediates of the monomer synthesis, the N-(3,4-bis(decyl-oxy)benzoyl)-2-aminoethanol **5** and the N-methyl-2-(3,4-bis(decyloxy)-phenyl)-2-oxazolinium trifluoromethanesulfonate **8**, exhibit liquid crystalline character. The thermal properties of the intermediates and the monomer are given in Table 2.

The optical texture of the N-substituted ethanolamide **5** between crossed polarizers is given in Figure 2a. It shows well pronounced spherulitic domains. The reason for the unexpected mesogenic behaviour of this compound must be the presence of the terminal hydroxy group, because the substitution of the hydroxy group with chloride, which leads to the N-substituted chloroethylamide **6**, causes the complete loss of mesogenity. On the other hand, in our opinion a single hydroxy group alone cannot be the reason of liquid crystallinity. There are examples in the literature were such a terminal OH-group results in mesomorphism only in the presence of other hydrogen bond proton-acceptors, e.g. OH-groups [15] or cyano and nitro groups [16]. Therefore it seems reasonable that the amido group together with the terminal hydroxy group must be responsible for the formation of the mesophase.

In contrast, the ionic oxazolinium trifluoromethanesulfonate **8** exhibits a

TABLE 2. Transition temperatures (in °C) and, in brackets, enthalpies (in $kJ \cdot mol^{-1}$) of compounds **4** - **8**. C: crystalline phase; M: mesophase; I: isotropic phase; [ ]: monotropic.

compound	C		M		I
4	•	49.8 (37.3)	-		•
5	•	85.6 (34.2)	•	[79.6 (1.2)]	•
6	•	104.1 (64.6)	-		•
7	•	47.6 (42.6)	-		•
8	•	89.5 (57.8)	•	[77.6 (0.8)]	•

homeotropic orientation of the mesophase. Birefringence can only be observed at phase borders, i.e. between the liquid and air bubbles (Figure 2b). This behaviour is well known for smectic phases [17]. The appearance of mesomorphism in general can here be explained by coulombic interactions. Beside the mentioned examples of ionic mesogens like low molecular and polymeric compounds with ammonium groups [5, 9], further liquid crystals are known, where ionic heterocyclic rings are responsible for the existence of mesomorphism [18]

As expected, the polymers **9** and **10** show liquid crystallinity. Their transition temperatures are given in Table 3. The products do not exhibit any crystalline phase, i. e. the mesophase can be frozen in above room temperature at 52 °C, resp. 38 °C.

The optical textures of the polymers are less pronounced than that of the monomer **5**, however spherulitic domains can clearly be recognized (Figure 3).

Those spherulitic textures are known for columnar mesophases [19]. However, at a first glance, the linear structure of the polymers gives no reason for such an arrangement. X-ray studies should elucidate this problem.

Because of the lack of classical, formanisotropic mesogenic unities (e.g. rods or discs) and supramolecular mesomorphism inducing hydrogen bonding or coulombic forces, it seems to us that a separation between the polar backbone and the apolar alkoxy side chains is responsible for the observed liquid crystallinity. Furthermore, in the presence of the used 'two chain' side groups the amido

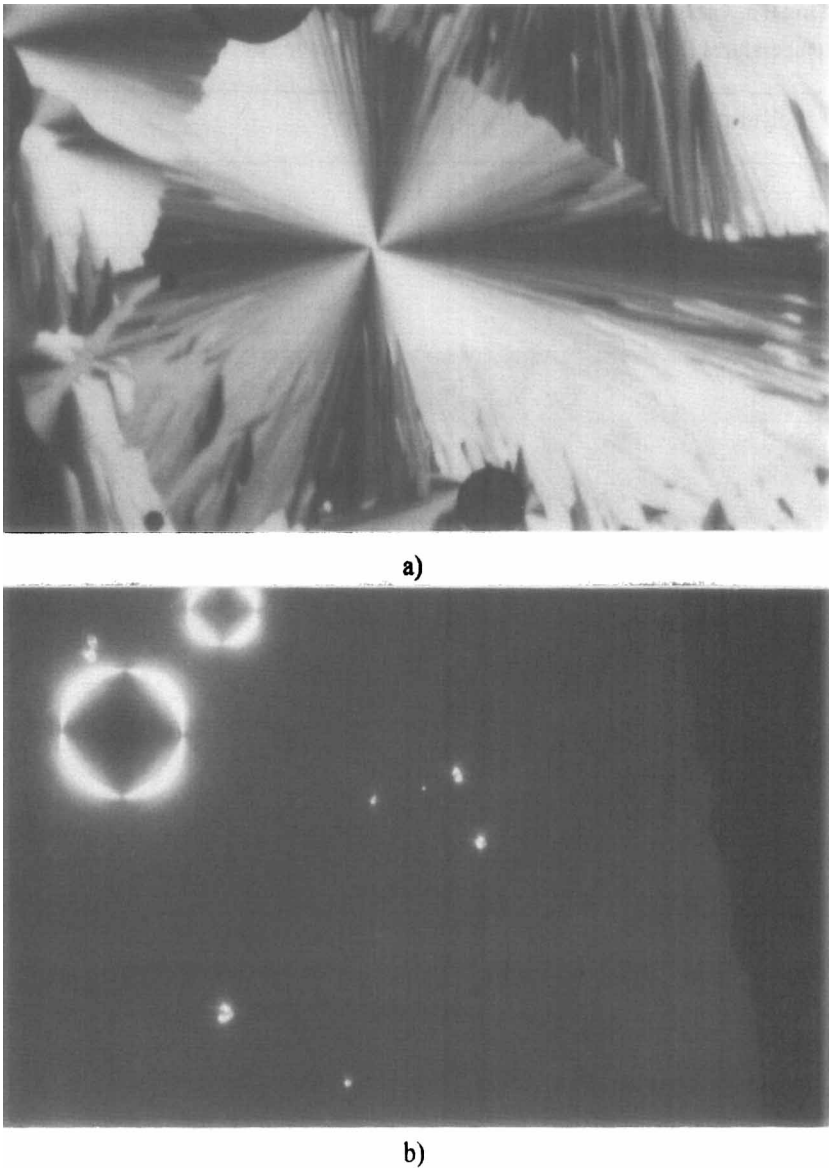


FIGURE 2. Optical textures of compounds **5** and **8** (between crossed polarizers); a) compound **5**, on cooling at 81.6°C, b) compound **8**, on cooling at 79.4°C

TABLE 3. Glass transition temperatures T_g (in °C), ΔC_p (in $J \cdot g^{-1} \cdot K^{-1}$) and clearing temperatures (in °C) of compounds **9** and **10**. M: mesophase; I: isotropic phase.

polymer	T_g	ΔC_p	M		I
9	52	0.26	●	103.3	●
10	38	0.34	●	86.1	●

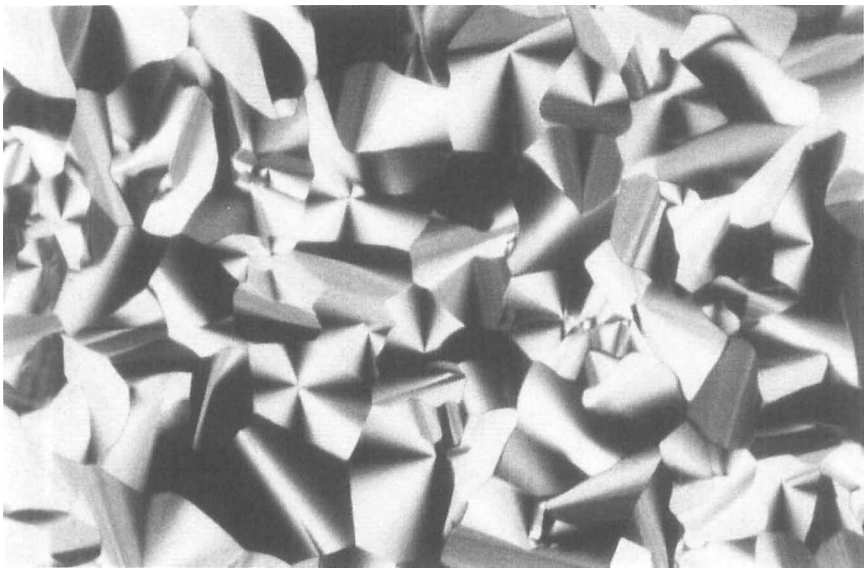


FIGURE 3. Optical texture of polymer **10** (between crossed polarizers), on cooling at 99.7°C

ethylene unities in the main chain apparently stiffen the backbone just in such an extent to allow mesomorphism but to avoid crystallinity. This behaviour is in contrast to the exclusive existence of a crystalline phase in LPEI samples with potential mesogenic, rodlike side groups descibed by Gramain et al. [10]. Our results show that the chemical architecture of the LPEI chain alone cannot directly

be responsible for a development of crystalline order. Either the lack of classical, rodlike side groups or the lower molar mass of the LPEI backbone or both should lead in our case to polymers exhibiting a liquid crystalline phase which is in the glassy state at room temperature.

4. CONCLUSION

In conclusion, we showed for the first time that the cationic polymerization of substituted 2-oxazolines is an appropriate way to new liquid crystalline side chain polymers with a linear poly(ethyleneimine) backbone. The advantages of this method, the living character of the polymerization reaction and the possibility of functionalizing termination to macromonomers, could be demonstrated in this work.

The unexpected mesomorphism of the two intermediates **5** and **8** shows the ability of supramolecular interactions to induce mesogenic behaviour in such molecular structures, which themselves do not seem to be appropriate for achieving liquid crystallinity.

The mesomorphism of the polymers **9** and **10** can not be explained in common structural terms. Thus, the combination of a polymer backbone with a certain flexibility and an a-priori non-mesogenic side group R (cf. Scheme 1), both of them neither with an extensive formanisotropic molecular unit nor with the possibility of extended supramolecular interactions, leads nevertheless to thermotropic stable mesophases. Additionally, the spherulitic textures indicate a mesophase structure, which seems to be in contrast to a linear, flexible molecular shape of the polymers. Ongoing studies on the mesophase structure as well as on chemical parameters, i.e. higher monomer/initiator ratios, variation of the side groups and the radical copolymerization of the macromonomer, will be reported in the future.

ACKNOWLEDGMENTS

We would like to thank Prof. Dr.-Ing. O. Nuyken and Dr. A. Groß for fruitful discussions. Furthermore, we gratefully acknowledge the financial support of the Deutsche Forschungsgemeinschaft (DFG La 662/1-2).

REFERENCES

[1] G. Lattermann, Liq. Crystals. **6**, 619 (1989)

[2] G. Lattermann, Mol. Cryst. Liq. Cryst. **182B**, 299 (1990)

[3] G. Lattermann, S. Schmidt, R. Kleppinger, J.H. Wendorff, Adv. Mater. **4**, 30 (1992)

[4] G. Lattermann, S. Schmidt, B. Gallot, J. Chem. Soc., Chem. Comm. **1992**, 1091

[5] a) V. Buscio, P. Corradini, V. Vacatello, J. Phys. Chem. **86**, 1033 (1982); b) C. M. Paleos, G. Margomenou-Leonidopoulou, A. Malliaris, Mol. Cryst. Liq. Cryst. **161**, 385 (1988); c) E. Alami, H. Levy, R. Zana, P. Weber, A. Skoulios, Liq. Cryst. **13**, 201 (1993)

[6] S. Schmidt, G. Lattermann, R. Kleppinger, J.H. Wendorff, Liq. Crystals **16**, 693 (1994)

[7] U. Stebani, G. Lattermann, R. Festag, M. Wittenberg, J.H. Wendorff, Adv. Mater. **6**, 572 (1994), Correction: Adv. Mater. **10**, 790 (1994)

[8] G. Lattermann, U. Stebani, 15th ILCC Budapest 1994, Vol. **I**, p. 18 (1994)

[9] a) S. Ujiie, K. Iimura, Polymer J. **25** 4, 347 (1993); b) S. Ujiie, K. Iimura, Chem. Lett. **11**, 1969 (1991); c) S. Ujiie, K. Iimura, Chem. Lett. **6**, 995 (1990)

[10] P. Masson, B. Heinrich, Y. Frère, P. Gramain, Macromol. Chem. Phys. **195**, 1199 (1994)

[11] A. Groß, PhD thesis, Bayreuth 1994, O. Nuyken, A. Groß, G. Maier, in preparation

[12] G. Staufer, G. Lattermann,Makromol. Chem. **192**, 2421 (1991)

[13] S. Kobayashi, T. Mizutani, T. Saegusa, Makromol. Chem. **185** ,441 (1984),

[14] H. Wenker, J. Am. Chem. Soc. **60**, 2152 (1938)

[15] a) F. Hentrich, C. Tschierske, H. Zaschke, Angew. Chem. Int. Ed. Engl. **30**, 440 (1991); b) N. Hoshino, H. Takahashi, Y. Matsunaga; H. Okamoto, T. Mitani, Mol. Cryst. Liq. Cryst. **216**, 265 (1992)

[16] A. C. Griffin, S. R. Vaidya, Mol. Cryst. Liq. Cryst. **173**, 85 (1989)

[17] G. Staufer, M. Schellhorn, G. Lattermann, Liq. Crystals, 1995, in press

[18] a) M. Veber, P. Sotta, P. Davidson, A. M. Levelut, C. Jallabert, H.

Strzelecka, J. Phys. France **51**, 1283 (1990); b) M. Veber, C. Jallabert, H. Strzelecka, O. Julien, P. Davidson, Liq. Crystals **8**, 775 (1990)

[19] C. Destrade, H. Gasparoux, P. Foucher, Nguyen Huu Tinh, J. Malthête, J. Jacques, J. chim. phys. **80**, 137 (1983)