

Scientific paper

# Thermotropic Liquid Crystalline $\alpha$ -(bis(2-hydroxyethyl)amino)- $\omega$ -(4'-nitroazobenzene-4-oxy) Alkane Hydrochlorides

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## Abstract

We investigated the liquid crystalline hydrochlorides  $\alpha$ -(bis(2-hydroxyethyl)amino)- $\omega$ -(4'-nitroazobenzene-4-oxy)alkanes with different spacer lengths (2, 4, 6, 8, and 10 methylene units). LC properties were determined by thermal analysis (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD). DSC thermograms exhibit only melting peak with no LC transitions. LC phase was observed with POM and confirmed by XRD. All hydrochlorides form a smectic phase that is stable up to 220 °C where isotropization proceeds simultaneously with degradation.

**Keywords:** Liquid crystalline, hydrochlorides, thermotropic, diethanolamine.

## 1. Introduction

Amines with mesogenic group have been used to prepare liquid crystalline polymers,<sup>1,2</sup> complexes with monomeric or polymeric organic acids,<sup>3–6</sup> and LC quaternary ammonium salts.<sup>7–11</sup> Many LC quaternary ammonium salts and hydrochlorides have already been synthesized.<sup>12</sup> According to literature amine hydrochlorides with long aliphatic chains have mainly been synthesized, some of them were liquid crystalline.<sup>13–15</sup> LC amine hydrochlorides with a rigid mesogenic group, which are the focus of this work, have not been the subject of intensive research work so far. Recently, we synthesized LC hydrochlorides based on diethanolamine having a mesogenic methoxybiphenyl group.<sup>16</sup> Interesting field of application for this kind of hydrochlorides is modification of layered silicate such as montmorillonite. Various 4-cyano-(4'-biphenyloxy)alkane ammonium hydrochlorides have been used for this purpose in order to prepare polymer nanocomposites for optical applications.<sup>17</sup>

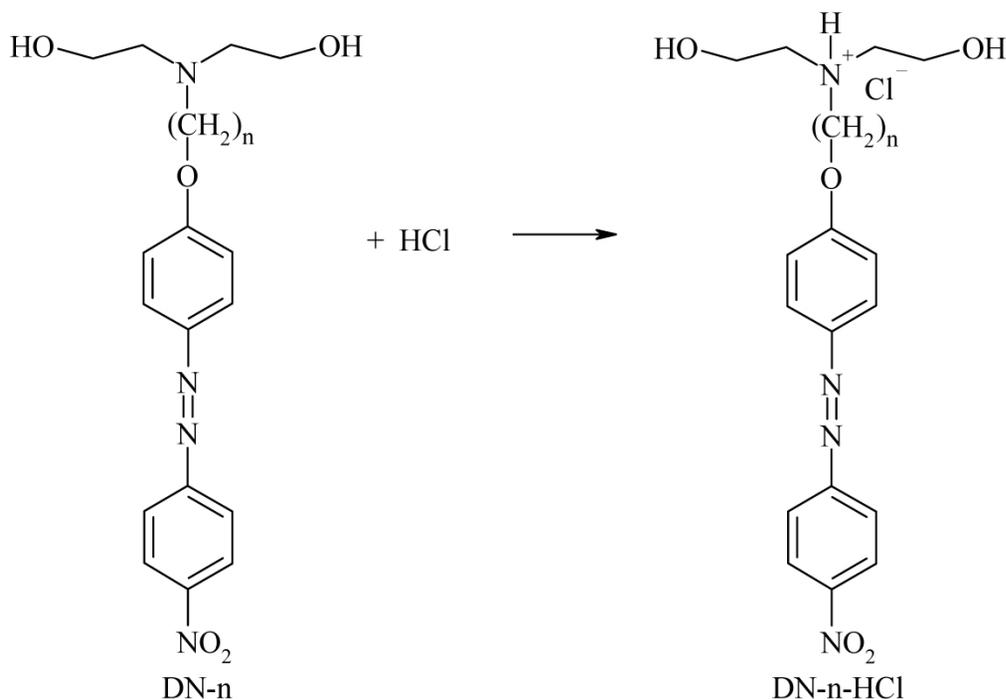
Liquid crystalline materials containing mesogenic azobenzene groups are more interesting than those with biphenyl groups, due to their possible applications in nonlinear optics, as well as in the opto-electronic and reversible data storage materials area.  $\alpha$ -(Bis(2-hydroxyethyl)amino)- $\omega$ -(4'-nitroazobenzene-4-oxy)alkanes (DN- $n$ ,  $n$  = number of methylene units) have already

been used as diols in the synthesis of liquid crystalline polyurethanes.<sup>18,19</sup> Ionic complexes of DN-6 with acids as poly(vinylsulfonate) and HBr have also been synthesized. The results showed increased thermal stability of the smectic phase of the ionic complex compared to DN-6.<sup>20</sup>

This paper focuses on the thermal and LC properties of the synthesized  $\alpha$ -(bis(2-hydroxyethyl)amino)- $\omega$ -(4'-nitroazobenzene-4-oxy)alkane hydrochlorides (DN- $n$ -HCl,  $n$  = number of methylene units), which will be further used for modification of montmorillonite<sup>21</sup> and LC nanocomposite preparation.

## 2. Experimental

The synthesis of  $\alpha$ -(bis(2-hydroxyethyl)amino)- $\omega$ -(4'-nitroazobenzene-4-oxy)alkanes (DN- $n$ -diol) is described elsewhere.<sup>18</sup> The synthesis of diol hydrochlorides (DN- $n$ -HCl,  $n$  = 2, 4, 6, 8, and 10) was conducted as described in a previous paper<sup>16</sup> by dissolving DN- $n$ -diol (1 g) in distilled tetrahydrofuran (10 g). Concentrated hydrochloric acid was added in an excess of 20 mol %. DN- $n$ -HCl precipitated immediately and the reaction mixture was left at room temperature for 1 h. After filtration the product was dried for 24 h under P<sub>2</sub>O<sub>5</sub> in vacuum at 60 °C. The reaction is depicted in scheme 1.



**Scheme 1:** The quaternization of DN-*n* (*n* = 2, 4, 6, 8, 10) with hydrochloric acid.

The yield of DN-*n*-HCl which precipitated from THF in a form of orange to red powder or small crystals was 70–85%.

The structure of DN-*n*-HCl was confirmed by <sup>1</sup>H NMR and <sup>1</sup>H NMR COSY spectroscopy. <sup>1</sup>H NMR spectra were recorded at 25 °C on a Varian VXR-300 spectrometer using DMSO-*d*<sub>6</sub> as the solvent and TMS as the internal standard. The NMR spectra of DN-*n*-HCl are similar to the spectra of DN-*n* diols.<sup>18</sup> They exhibit significant changes only in the vicinity of the quaternary nitrogen atom. The signals of DN-4-HCl to DN-10-HCl are assigned as follows: 10.1–9.6 ppm (broad s, 1H, H-N<sup>+</sup>), 8.4 (d, 2H, aromatic protons next to NO<sub>2</sub>), 8.0 (dd, 4H, aromatic protons beside N=N), 7.2 (d, 2H, aromatic protons beside O-alkyl chain), ≈5.4 (broad s, 2H, OH), 4.2–4.1 (t, 2H, -N<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-O-CH<sub>2</sub>-), 3.75 (t, 4H, -CH<sub>2</sub>OH), 3.40–3.25 (m, 4H, N<sup>+</sup>-(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>), 3.15 (m, 2H, N<sup>+</sup>-CH<sub>2</sub> - spacer), 1.7 (m, 4H, O-CH<sub>2</sub>-CH<sub>2</sub> and N<sup>+</sup>-CH<sub>2</sub>-CH<sub>2</sub>), 1.2–1.5 (m, 4–12H, inner CH<sub>2</sub> groups of aliphatic spacer). The assignment of DN-2-HCl is slightly different. The signals of aromatic protons are on the same positions while the others are assigned as: 4.6 (t, 2H, -N<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-O-CH<sub>2</sub>-), 3.85 (t, 4H, -CH<sub>2</sub>OH), 3.75 (m, 2H, N<sup>+</sup>-CH<sub>2</sub> - spacer), 3.40 (m, 4H, N<sup>+</sup>-(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>).

Differential scanning calorimetry (DSC) analysis was performed on a Perkin-Elmer Pyris 1 calorimeter. The samples were heated twice and subsequently cooled with the heating and cooling rate 10 K/min. The temperature range varied for different samples to prevent unnecessary decomposition within DSC cell.

Optical textures were obtained using a Carl Zeiss polarizing optical microscope Stemi SV6 equipped with an MC 80 microscope camera and a Mettler Toledo FP82 hot stage. X-ray diffraction patterns were taken on a Siemens D-5000 diffractometer using Cu K<sub>α</sub> radiation ( $\lambda = 1.54 \text{ \AA}$ ) in 0.04° steps from 0.5–35° (in 2 $\theta$ ) with 4 s per step.

## 3. Results and Discussion

### 3. 1. Thermal Properties

The DSC curves of all DN-*n*-HCl taken during the first heating scan are shown in Figure 1. They all exhibit one or several recrystallization peaks before melting. An exothermic transition is even observed in DN-8-HCl at 104 °C. Most of the hydrochlorides exhibit only one crystallization peak on cooling, while hydrochloride with 4 methylene units exhibit second recrystallization peak at 52.2 °C.

Since DSC curves did not indicate any LC transitions we heated the samples to 250 °C. Only exothermic decomposition was observed above 200 °C. There were no peaks observed on cooling and a second heating of decomposed samples. According to the DSC results, DN-*n*-HCl did not exhibit LC transitions.

The second heating scans of DN-*n*-HCl are shown in Figure 2. Hydrochlorides with low (2 and 4) and high number (10 and 12) of methylene units exhibit single melting peak while the melting of others is more complex.

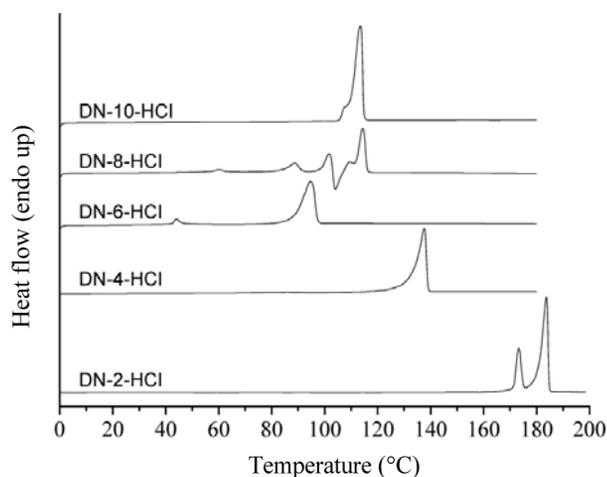


Figure 1: DSC thermograms of DN-*n*-HCl taken during the first heating.

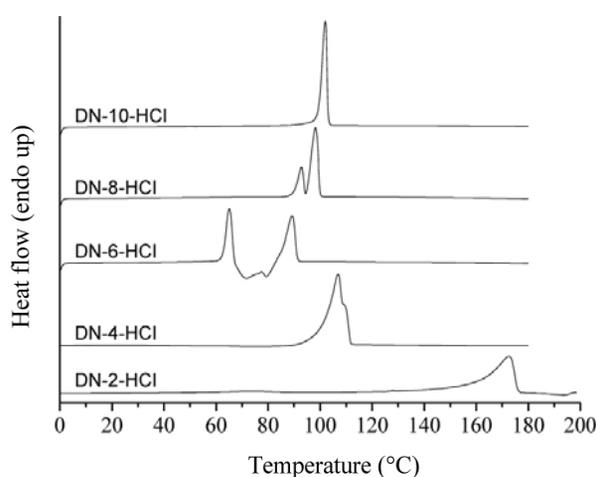


Figure 2: DSC thermograms of DN-*n*-HCl taken during the second heating.

DN-6-HCl exhibits several exo- and endothermic transitions while DN-8-HCl exhibits one recrystallization and melting peak. All melting temperatures and melting enthalpies in the second heating scan are lower than in the first scan (Table 1). This may have been either a material property or just a consequence of the small degree of thermal decomposition during the first heating scan. Therefore, we measured the DSC of DN-10-HCl in the temperature range between 0–120 °C. This should prevent decomposition and its influence on thermal properties in the second heating run. Nevertheless, similar results were obtained. The melting peak in the second run was 0.4 °C higher and the melting enthalpy 0.6 J/g higher than in the first experiment. According to this result degradation above the melting point is possible but it is not fast at the measured temperatures. No weight loss was observed at this experiment but nevertheless, keeping the samples above the melting point for longer period of time could lead to extensive degradation.

### 3. 2. Liquid Crystalline Properties

Liquid crystalline properties were observed during the heating the samples on POM. All samples melted at

the temperatures determined by DSC. Contrary to expectations, the melts were not isotropic. A sanded texture appeared, which was also observed in hydrochlorides having methoxybiphenyl mesogenic group.<sup>16</sup> The isotropization temperatures were at 210–227 °C, increasing with the number of methylene units. At those temperatures decomposition proceeded as well, which was observed as bubble formation.

The sanded texture might not be characteristic for any LC phase since a similar sanded texture has also been observed in a mixture of an isotropic polyester melt and crystalline cyclic ester compounds.<sup>22</sup> Therefore, the existence of LC phase was confirmed by X-ray diffraction.

Since the melting temperatures of DN-2-HCl and DN-4-HCl are high, which might lead to unwanted decomposition and pollution of the X-ray equipment, the XRD experiments were made for hydrochlorides with 6–10 methylene units only. The X-ray diffractograms recorded at 100 °C (DN-6-HCl) or 120 °C (DN-8-HCl and DN-10-HCl) are shown in Figure 3. In the low angle region there are two Bragg reflections of the first and second order indicating formation of the smectic phase. The position of the reflections corresponds to a layer spacing of 3.09 nm (DN-6-HCl), 3.39 nm (DN-8-HCl), and

Table 1: Thermal properties of DN-*n*-HCl

	DN-2-HCl		DN-4-HCl		DN-6-HCl	
	$T_m$ (°C)	$\Delta H$ (J/g)	$T_m$ (°C)	$\Delta H$ (J/g)	$T_m$ (°C)	$\Delta H$ (J/g)
1 <sup>st</sup> heating	184.5	110.8	137.9	84.5	94.8	69.0
cooling	150.0	-56.4	91.4	-31.0	56.1	-19.7
2 <sup>nd</sup> heating	173.8	67.7	107.4	70.0	89.2	26.6
	DN-8-HCl		DN-10-HCl			
	$T_m$ (°C)	$\Delta H$ (J/g)	$T_m$ (°C)	$\Delta H$ (J/g)		
1 <sup>st</sup> heating	114.2	32.5*	113.2	95.4		
cooling	78.0	-36.5	92.3	-34.4		
2 <sup>nd</sup> heating	98.0	28.1	101.7	35.3		

\* Approximate value due to overlapping peaks.

3.71 nm (DN-10-HCl). Comparing the latter value with the calculated length of the DN-10 molecule (3.09 nm)<sup>23</sup> increased for the ionic diameter of Cl (0.362 nm),<sup>8,24</sup> we can assume that hydrochlorides form an interdigitated monolayered smectic phase. The molecules are laterally arranged head to tail as observed in *N*-alkylpyridinium halides.<sup>8</sup> The exact type of smectic phase could not be determined on the basis of the X-ray spectra of unoriented samples.

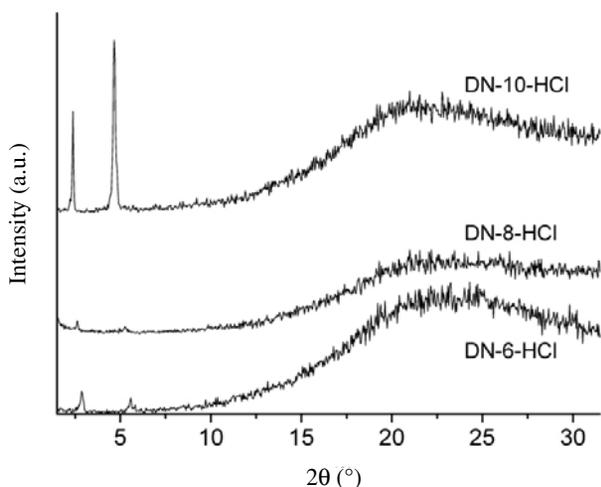


Figure 3: X-ray diffractograms of DN-*n*-HCl in LC phase.

Although the spectra were recorded using the same experimental parameters the intensities of the diffraction peaks differ greatly. The peaks for DN-8-HCl are hardly visible due to the bad stacking of the layers one over the other, or to a large diffusion of the molecules from one layer to the next.

According to DSC results both DA-8-HCl and DA-6-HCl undergo endothermic and exothermic processes before melting on the second heating run (Figure 2). To gain information about these processes the samples were cooled from the LC phase (120 and 100 °C, respectively) to 40 °C at a cooling rate of 10 K/min and reheated to 93 °C (DA-8-HCl) or 67 and 75 °C (DA-6-HCl). X-ray diffractograms recorded at these temperatures gave similar results. X-ray diffractograms of DN-6-HCl are shown in Figure 4 as a representative example.

At 40 °C there are two Bragg reflections in the small angle region at the same position as in the LC phase, but the intensity is approximately four times higher (Fig. 4, diffractogram 1). In the wide angle region there are several broad peaks at approximately the same positions as in diffractograms 2 and 3. It seems that on cooling a part of the sample exists in a frozen smectic phase and another part in a not well-defined crystalline phase. At 67 °C, which is at the end of the first endothermic peak on the DSC curve, the diffractions of the frozen LC smectic pha-

se disappeared and several new diffractions appeared in the whole measured range (Fig. 4, diffractogram 2). In the small angle region there are three Bragg reflections of the first, second and third order indicating the formation of a smectic crystalline phase with a layer spacing of 4.88 nm. According to the increase in layer spacing we can assume that bilayered smectic crystals were formed. At 75 °C the new diffractions became sharper and more intense. It seems that crystallization proceeds in the temperature ran-

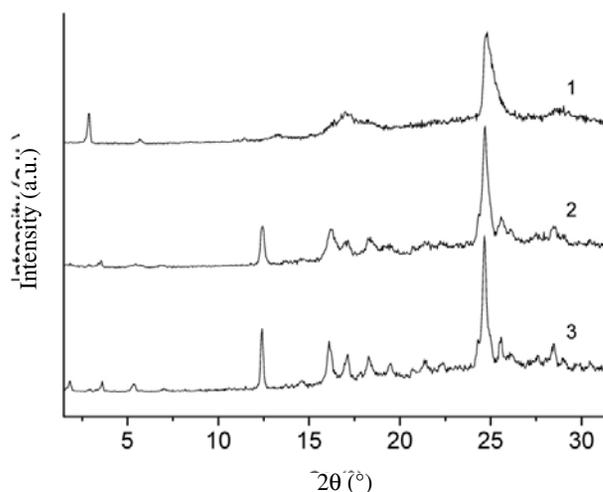


Figure 4: X-ray diffractograms of DN-6-HCl: (1)  $T = 40$  °C, after cooling from LC phase, (2) reheated to  $T = 67$  °C, (3) reheated to 75 °C.

ge 67–82 °C, which is in agreement with DSC measurements.

The second heating DSC curve of DN-10-HCl exhibits no recrystallization peak but the melting temperature is 11.5 °C lower and the melting enthalpy is only a third of the original value. In Figure 5, the X-ray diffractograms of DN-10-HCl recorded at room temperature before heating

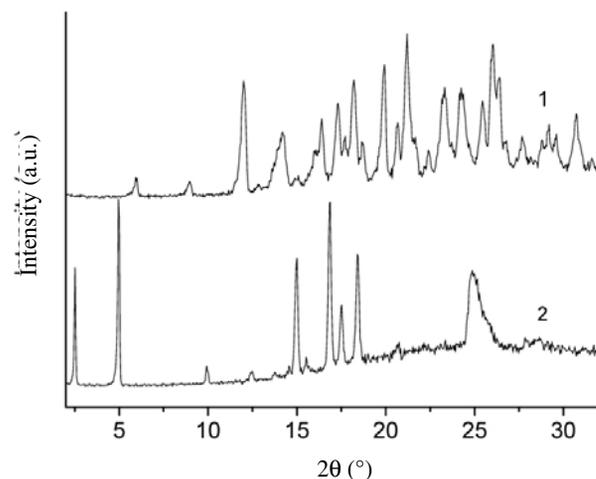


Figure 5: X-ray diffractograms of DN-10-HCl. (1) crystalline (2) after cooling from LC phase to room temperature.

to the LC phase (diffractogram 1) and after cooling from the LC phase (diffractogram 2) are shown. On cooling from the LC phase new smectic crystals were formed with a layer spacing of 3.48 nm, which is 0.23 nm thinner than in the LC phase. The smectic crystals formed on cooling from the LC phase melt at a lower temperature than crystals formed during synthesis.

## 4. Conclusions

Liquid crystalline properties of the synthesized  $\alpha$ -(bis(2-hydroxyethyl)amino)- $\omega$ -(4'-nitroazobenzene-4-oxy)alkane hydrochlorides with different spacer lengths (2, 4, 6, 8 or 10 methylene units) were characterized by DSC, polarizing optical microscopy, and X-ray diffraction.

The results show that it is important to use complementary techniques to determine whether a material is liquid crystalline or not. According to the DSC curves all hydrochlorides are exclusively crystalline. However, as shown by POM and XRD, the LC phase is formed on melting and turns to an isotropic melt at temperatures above 220 °C, which is also where degradation proceeds. Since the enthalpy of the LC-I transition is much smaller than the enthalpy of decomposition the transition could not be observed by DSC. Hydrochlorides form a disordered monolayered smectic A or smectic C phase. The exact type of smectic phase could not be determined on the basis of the X-ray spectra of unoriented samples.

## 5. Acknowledgements.

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## 6. References

1. W. Mormann, M. Brocher, *Polymer* **1998**, *39*, 4905–4910.

2. G. Schwarz, S. J. Sun, H. R. Kricheldorf, M. Ohta, H. Oikawa, A. Yamaguchi, *Macromol. Chem. Phys.* **1997**, *198*, 3123–3135.
3. S. Ujiie, K. Imura, *Chem. Lett.* **1994**, *1*, 17–20.
4. J. F. Gohy, R. Jérôme, *Prog. Polym. Sci.* **2001**, *26*, 1061–1099.
5. M. Marin, L. Banos, A. Moreno, G. Burillo, T. Ogawa, *Polym. Bull.* **1995**, *34*, 227–233.
6. S. Ujiie, Y. Yano, S. Tanimoto, M. Sato, *Kobunshi Ronbunshu*, **1999**, *56*, 385–389 (*Chem. Abstr.* **1999**, *131*, 185472).
7. A. Terreros, P. A. Galera Gomez, E. López Cabarcos, A. Müller, *Colloids Surf., A* **2000**, *164*, 47–53.
8. D. Navarro-Rodriguez, Y. Frere, P. Gramain, D. Guillon, A. Skoulios, *Liq. Crystals* **1991**, *9*, 321–335.
9. M. Bujan, N. Vdović, N. Filipović-Vinceković, *Colloids Surf., A* **1996**, *118*, 121–126.
10. D. J. Abdallah, L. D. Lu, T. M. Cocker, R. E. Bachman, R. G. Weiss, *Liq. Cryst.* **2000**, *27*, 831–837.
11. M. Arkas, C. M. Paleos, A. Skoulios, *Liq. Cryst.* **1997**, *22*, 735–742.
12. K. Binnemans, *Chem. Rev.* **2005**, *105*, 4148.
13. A. V. A. Pinto, I. Vencato, H. A. Gallardo, Y. P. Mascarenhas, *Mol. Cryst. Liq. Cryst.* **1987**, *149*, 29–40.
14. K. Iwamoto, Y. Ohnuki, K. Sawada, M. Seno, *Mol. Cryst. Liq. Cryst.* **1981**, *73*, 95–103.
15. V. Busico, A. Scopa, M. Vacatello, *Z. Naturforsch., A: Phys. Sci.* **1982**, *37a*, 1466–1468.
16. M. Huskić, M. Žigon, *Liq. Cryst.* **2002**, *29*, 1217–1222.
17. M. Kawasumi, N. Hasegawa, A. Usuki, A. Okada, *Appl. Clay Sci.* **1999**, *15*, 93–108.
18. M. Brecl, T. Malavašič, *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2871–2888.
19. M. Brecl, G. Ambrožič, M. Žigon, *Polym. Bull.* **2002**, *48*, 151–158.
20. S. Ujiie, K. Imura, *Macromolecules* **1992**, *25*, 3174–3178.
21. I. Brnardić, M. Huskić, M. Žigon, M. Ivanković, *J. Non-Cryst. Solids* **2008**, *354*, 1986–1991.
22. M. Huskić, M. Žigon, *Polymer* **2003**, *44*, 6187–6193.
23. H. Qiu, M. Li, X. Chen, F. Jing, E. Zhou, *Liq. Cryst.* **1998**, *25*, 419–425.
24. J. M. R. Génin, C. Ruby, *Solid State Sci.* **2004**, *6*, 705–718.

## Povzetek

Sintetizirali in analizirali smo tekočerkristalinične (LC) hidrokloride  $\alpha$ -(bis(2-hidroksietil)amino)- $\omega$ -(4'-nitroazobenzene-4-oksi)alkanov, z različnimi dolžinami alkilnih verig (2, 4, 6, 8, in 10 ogljikovih atomov). LC lastnosti smo določili s termično analizo (DSC), polarizacijskim optičnim mikroskopom (POM) in rentgensko difrakcijo (XRD). Z DSC termogrami smo določili taljenje hidrokloridov, nismo pa opazili LC prehodov. Nastanek LC faze v talini hidrokloridov smo ugotovili z optičnim mikroskopom in jo potrdili z XRD. Vsi hidrokloridi tvorijo smektično LC fazo, ki je stabilna do 220 °C, kjer izotropizacija poteka istočasno z degradacijo.