Liquid crystalline derivatives of oligoethylene-amines and -amino ethers with amide, ester, urea or urethane functions

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The mesomorphism of diethylenetriamine and triethylenetetramine derivatives, substituted with the 3,4-bis(decyloxy)benzoyl group ('two chain' substituent) *via* amide, ester, urea or urethane moieties, is described. Furthermore, different examples of related linear and cyclic oligoethyleneamino ethers are investigated and compared with the mesomorphism of the first group. Both lamellar smectic A and hexagonal columnar mesophases can be observed in linear compounds, depending on the length of the linear unit. A cyclic derivative displays a cubic phase. The conclusion is emphasized that the mesomorphism of these classes of compounds is caused by microphase separation.

Several groups have recently described liquid crystalline cyclic,[1–14] linear[12,13,15–17] and branched[13,18] oligo- or poly-alkyleneamides, which are an interesting class of mesogens because of several reasons: (i) they do not fulfil the criteria of conventional thermotropic mesomorphism, *i.e.* they do not exhibit a rigid, anisometric architecture of classical rod-like or disc-like single molecules (molecular mesogens); (ii) they cannot be classified in general as supramolecular mesogens, forming aggregates of non-mesogenic single molecules *via* strong interaction forces, *e.g.* hydrogen bonding, ionic or charge transfer forces; (iii) derivatives of the considered group of mesogenic oligo- or poly-alkyleneamines can either be converted to the corresponding ionic liquid crystals[18,19] or can be used as ligands in a variety of new groups of metallomesogens.[14,20–24] Here we describe materials which give evidence for (i) and (ii).

Results

Ester endgroup derivatives

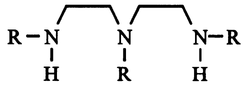
To investigate the influence of terminal hydrogen bonding on the mesophase structure of the 3,4-bis(decyloxy)benzoyl ('two chain') substituted diethylenetriamine **1** (2,2-tri)[15] and on a postulated ring closure[12,13] of the triethylenetetramine derivative **2** (2,2,2-tet),[16] we synthesized analogues of **1**, *i.e.* the monoester **3** (2,2-monoester), the diester **4** (2,2-diester) and the analogue of **2** with two ester endgroups **5** (2,2,2-diester).

Thermal behaviour. Polarizing microscopy and differential scanning calorimetry (DSC) measurements revealed monotropic mesophases for 2,2-monoester **3** and 2,2-diester **4** and an enantiotropic mesophase for 2,2,2-diester **5**. Their transition temperatures together with those of 2,2-tri **1**[15] and 2,2,2-tet **2**[16] are summarized in Table 1.

The monotropic mesophase of 2,2-monoester **3**, followed by a rapid crystallization, is detectable only under the polarizing microscope. In DSC measurements, only a slight shoulder on the crystallization peak appears (even at different heating rates). The 2,2-diester **4** exhibits crystalline phases only on the first heating, which do not reappear on further heating, *i.e.* the 'pseudo enantiotropic' mesophase can be frozen in below its glass temperature at $T_g = 5\,°C$ ($\Delta C_p = 0.98$ kJ mol^{-1} K^{-1}). 2,2,2-Diester **5** exhibits no crystalline phase from the beginning. It shows a glass transition temperature at $T_g = 18\,°C$ ($\Delta C_p = 1.29$ kJ mol^{-1} K^{-1}).

A comparison of the transition temperatures of **1** with **3** or **4** reveals that with a decreasing number of hydrogen bonds, the melting temperatures decrease. In **4**, the crystalline phases disappear after the first heating. Whereas 2,2,2-tet **2** exhibits the highest melting temperature of all the compounds shown in Table 1, crystalline phases are no longer detectable in the analogous 2,2,2-diester **5**. Although the clearing temperatures follow the same pattern, the mesophases do not disappear in compounds **3**, **4** and **5**, but instead become dominating in 'pseudo' enantiotropic **4** and enantiotropic **5**.

Under the polarizing microscope, for compounds **3** and **4** broken fan-shaped textures can be observed. The 2,2,2-diester **5** exhibits a broken spherulithic texture.



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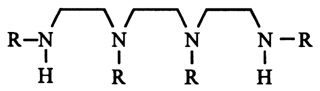

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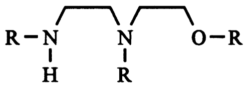

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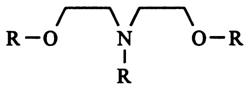

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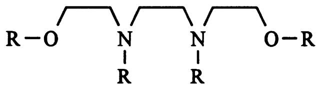

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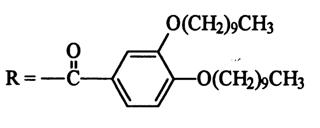


Table 1 Transition temperatures, ΔC_p values and ΔH values of compounds **1**, **2**, **3**, **4** and **5**; T_g, glass transition temperature; K, crystalline phases; M, mesophase; I, isotropic phase

compound	T_g/°C (ΔC_p/kJ mol^{-1} K^{-1})	K_1	transition temp/°C (ΔH/kJ mol^{-1})	K_2		K_3		M		I
1[a]	—					●	90.6 (65.9)	●	85.6[e] (2.4)	●
2[b]	52 (0.33)			●	59.0[c] (25.2)	●	93.5 (21.1)	●	104.0 (3.0)	●
3	—			●	52.0 (26.5)	●	83.0 (38.5)	●	66[d,e]	●
4	5 (0.98)	●	39.5[c]	●	53.5[c] (59.3)[f]	●	60.5[c] (0.8)	●	35.5[e] (2.6)	●
5	18 (1.29)							●	62.5 (5.1)	●

[a]Ref. 15. [b]Ref. 16. [c]Only on first heating. [d]Detectable only under the polarizing microscope. [e]Monotropic. [f]ΔH for K_1 and K_2.

Table 2 X-Ray data for compounds **1**, **2**, **4** and **5**

compound	distance[a]/Å d_{100}	d_{110}	d_{200}	d_{210}	d_{220}	d_{300}	d_{layer} (T/°C)	lattice constant a_{hex} (T/°C)
1[b]	30.1		15.1			10.1	30.2 (85)	
2[b]	28.4	16.8	14.6	11.2	8.4	9.7		33.6 (90)
4	30.6		15.4			10.2	30.7 (25)	
5	30.5	18.4	15.6	12.2		10.6		36.9 (20)

[a]d_{hk0}, lattice spacings; d_{layer}, layer distance. [b]Ref. 16, 25.

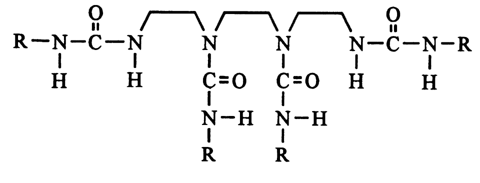
X-Ray investigations. The monotropic phase behaviour did not allow the determination of the mesophase structure of compound **3**. For **4** and **5** the results are summarized in Table 2, together with the values for **1** and **2**.[16,25]

Likewise to the analogous 2,2-tri **1**,[16] the presence of a lamellar smectic A mesophase in 2,2-diester **4**, which was deduced from the broken fan shaped texture, is supported by the first- to third-order reflections (d_{100}, d_{200} and d_{300}) in the diffractogram. In analogy to 2,2,2-tri **2**,[16] the 2,2,2-diester **5** displays a hexagonal columnar phase (Col$_h$), characterized by the additional d_{110} and d_{210} reflections.

Except for the influence on the transition temperatures, the formal exchange of amide *versus* ester endgroups, *i.e.* the impossibility for the formation of hydrogen bonding, has no further influence on the mesophase.

Derivatives with urea and urethane substituents

A second possibility for the investigation of the role of hydrogen bonding is not to reduce but to enhance the number of proton donors and acceptors. Therefore, we synthesized compounds **6** (2,2,2-urea) and **7** (2,2,2-urea/urethane), whose 'two chain' substituents are linked to the triethylenetetramine backbone *via* urea or urethane moieties instead of amide groups.



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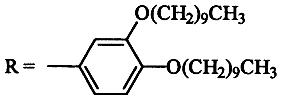
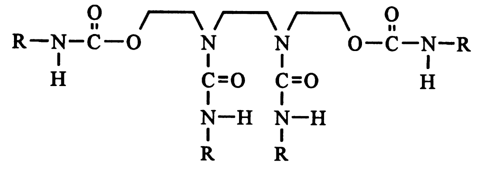




7

Thermal behaviour. Polarizing microscopy and DSC measurements revealed enantiotropic mesophases for both **6** and **7**. Their transition temperatures are summarized in Table 3.

With respect to **2**, compound **6** shows crystalline phases only on first heating, with a lower melting temperature. This behaviour is contrary to the expectation that a larger number of possible hydrogen bondings would favour crystallinity in **6** with respect to **2**. The clearing temperature of the mesophase, which can be frozen in at room temperature, is slightly raised by about 4 °C. The value of T_m for **7** is increased not only with respect to **2** but also to **6**, although the number of possible hydrogen bonds is decreased with respect to **6**. Although this behaviour would indicate a stabilized crystalline phase, it appears only on first heating. As a consequence, the mesophase can be frozen in at room temperature too. The clearing temperature for **7** is increased with respect to **2** and **6**. Apparently, the number of possible hydrogen bonds does not relate in a simple way to the thermal behaviour of linear oligoethylene amine derivatives.

Under the polarizing microscope both compounds exhibit spherulithic textures, as shown in Plates 1 and 2.

X-Ray investigations. Compounds **6** and **7** display hexagonal columnar mesophases (Col$_h$) with lattice parameters given in Table 4. With respect to 2,2,2-diester **5**, a_{hex} for **6** and **7** is found to be in the same range.

Apparently, the formation of a hexagonal columnar mesophase depends only on the number of substituents, *i.e.* four in **2**, **5**, **6** and **7**, independent of the nature of the linking groups between the backbone and the 'two chain' substituents and, in consequence, independent of the number of possible hydrogen bonds.

In the following, we investigate the consequence of further variations of the molecular structure of this type of mesogen.

Derivatives with oxobridges

We synthesized the linear analogues of 2,2-tri, 2,2,2-tet and 2,2,2-urea with oxobridges, *i.e.* compounds **8**, **9** and **11**. Furthermore, the cyclic ethyleneamino ethers **12** and **14** with a different number of amide groups and **13** with urea groups were investigated. To compare the influence of the number of alkoxy chains, a 'three chain' compound **10**, related to **9**, was synthesized.

Table 3 Transition temperatures, ΔC_p values and ΔH values in 2,2,2-urea **6** and 2,2,2-urea/urethane **7**; T_g, glass transition temperature; K, crystalline phases; M, mesophase; I, isotropic phase

		transition temp/°C (ΔH/kJ mol^{-1})						
compound	T_g/°C (ΔC_p/kJ mol^{-1} K^{-1})	K_1		K_2		Col_h		I
6	44 (0.57)	•	57.0^a	•	75.0^a (38.9)^b	•	108.0 (1.6)	•
7	39 (0.56)			•	109^a	•	115.0 (2.7)	•

[a] Only on first heating. [b] ΔH for K_1 and K_2.

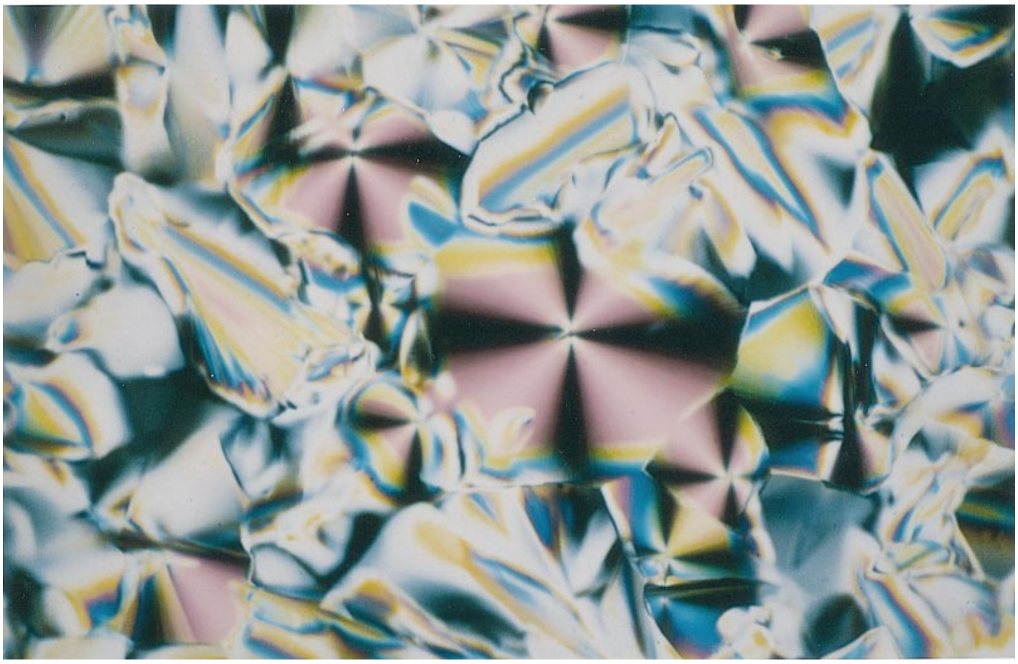


Plate 1 Optical texture of the mesophase after cooling from the isotropic phase for 2,2,2-urea **6**, $T = 106$ °C

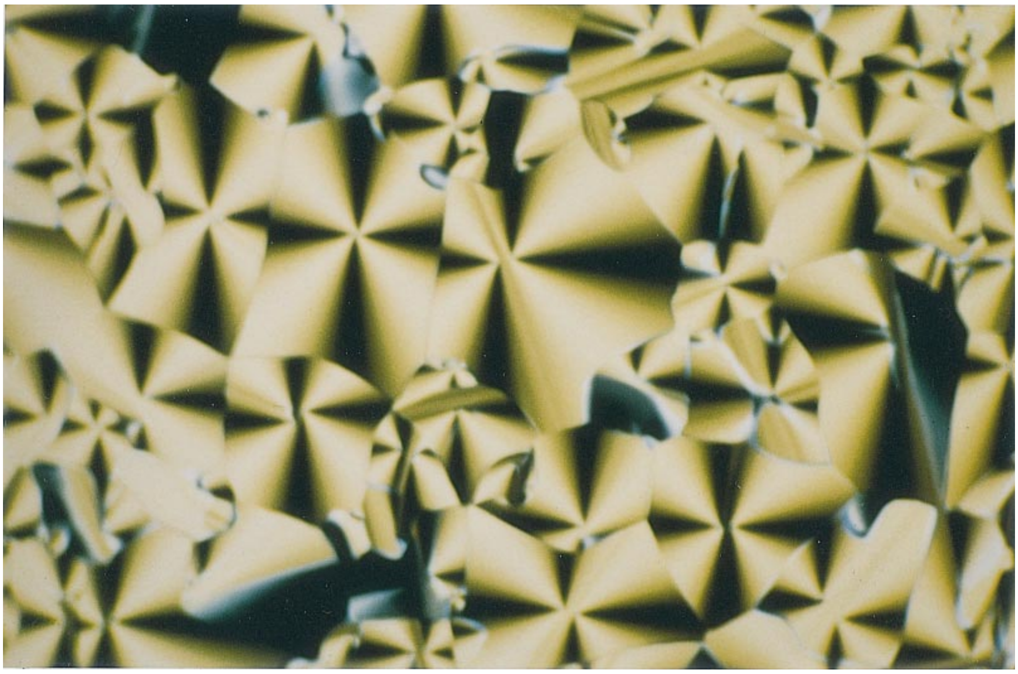


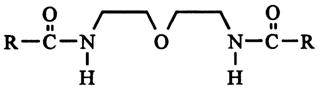
Plate 2 Optical texture of the mesophase after cooling from the isotropic phase for 2,2,2-urea/urethane **7**, $T = 100$ °C

Thermal behaviour. None of the linear oligoethyleneamino ethers **8**–**11** displays mesomorphism, as shown in Table 5. Comparing the linear compounds **8** with **1** and **9** with **2**, we observe that with an equal number of possible hydrogen bonds, the compounds with oxobridges exhibit higher melting temperatures. Going from **8** to **9** and maintaining a constant number of substituents and possible hydrogen bonds, increasing the number of oxobridges in **9** with respect to **8** increases the melting temperature. Comparing cyclic derivatives **12** and **14** with **15**, we observe that, contrary to the linear compounds,

Table 4 X-Ray data for compounds **6** and **7**

compound	distance[a]/Å d_{100}	d_{110}	d_{200}	d_{210}	d_{300}	lattice constant a_{hex} (T/°C)
6	32.10	18.90	16.10	12.34	10.92	36.9 (85)
7	32.30	18.08	15.86	—	—	37.0 (100)

[a] d_{hk0}, lattice spacings.



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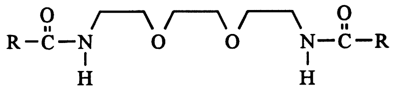

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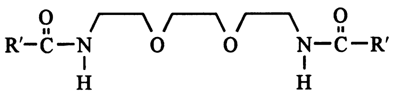

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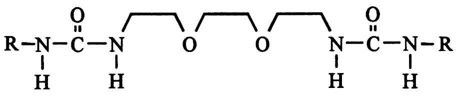

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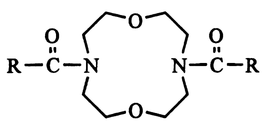

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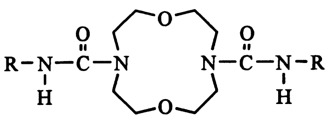

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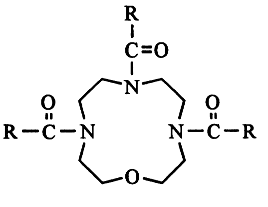

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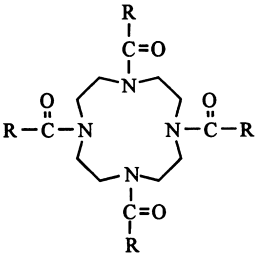

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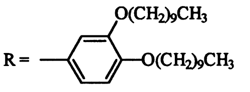

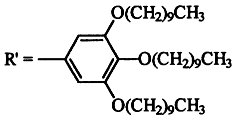

the presence of oxobridges in **12** and **14** decreases the melting temperatures.

Changing from amide to urea groups in linear compounds, *i.e.* from **2** to **6** or from **9** to **11**, decreases the melting temperatures, though the number of possible hydrogen bonds increases. Unlike linear derivatives, changing from amide groups in cyclic **12** to urea groups in **13** increases the melting temperature.

Introducing 'three chain' substituents in **10** instead of 'two chain' groups in **9** decreases the melting temperature.

For **8** compared to **1** and in **9** compared to **2**, the presence of only two 'two chain' substituents is apparently insufficient for mesophase formation. Neither increasing the number of decyl side chains going from **9** to **10** nor increasing the number of possible hydrogen bondings going from **9** to **11** is favourable for the formation of a mesophase.

Among the cyclic derivatives, compounds **12** and **13** are not liquid crystalline. Apparently, in **12** compared to the enantiotropic compounds **14** and **15**, the number of 'two chain' substituents is too small to induce mesomorphism, *i.e.* the minimum number is three substituents, as shown for compound **14**. Again, as with the linear compound **11**, increasing the number of possible hydrogen bonds going from **12** to **13** does not induce the formation of a mesophase.

Under a polarizing microscope, **14** exhibits an isotropic, viscous phase. At the 'clearing' temperature of 67 °C, which is indicated by a sharp peak in DSC measurements, a strong decrease in its viscosity can be observed under the microscope. These observations are typical for a cubic phase. Preliminary X-ray measurements in the very small mesophase range gave no information on the space group of the cubic phase. The tetrasubstituted cyclen derivative **15** has been shown to exhibit a hexagonal columnar mesophase (Col_h).[12]

The thermal behaviour of the derivatives with oxobridges demonstrates that a too small number of substituents with alkoxy chains does not favour the formation of a liquid crystalline phase, presumeably due to insufficient space filling in the outer sphere of the molecule. This factor seems to be dominant with respect to the influence of hydrogen bonds.

Discussion and Conclusion

Our results concerning oligoethylene-amine and -amino ether derivatives with decyloxy sidechains can be summarized as follows.

(i) In linear derivatives, the presence of oxobridges (compare **8** with **1**, **9** with **2** and **11** with **6**) increases the melting temperature, contrary to the behaviour of cyclic compounds (compare **12** and **14** with **15**). In both classes, an increasing number of oxobridges (compare **9** with **8** and **12** with **14**) increases the melting temperature.

(ii) In linear derivatives, changing from amide to urea groups (comparing **2** with **6** and **9** with **11**) decreases the melting temperature (in the case of **6** only on first heating), contrary to the behaviour of cyclic compounds (compare **12** with **13**). On first heating, compound **7** with urea/urethane functions exhibits the highest melting temperature with respect to **2** and **6**.

(iii) Comparing linear derivatives **1** with **4** and **2** with **5** it is evident that hydrogen bonding influences the transition temperatures, but is not essential for the appearance of a mesophase.

(iv) The existence of mesomorphism for the linear 2,2-tri compound **1** but not for analogous **8**, and for the cyclic analogue **14** but not for **12**, demonstrates that a minimum number of three 'two chain' substituents is necessary to obtain liquid crystallinity. Even additional hydrogen bonds in compound **11** with respect to **9** and in **13** with respect to **12**, or a larger number of decyl side chains at the endgroups in the 'three chain' compound **10**, are apparently not able to compensate for the two small number of side chains along the molecule, *i.e.* in this class of related compounds a minimum number of three 'two chain' substituents is the dominating factor for the existence of mesomorphism. The absence of mesomorphism in related sulfur-containing macrocyclic compounds with only 'two chain' substituents[26] seems to support these findings.

(v) By comparing the linear derivatives **1**, **3** and **4** (lamellar smectic A mesophases) with compounds **2**, **5**, **6** and **7** (hexagonal columnar mesophases), we can conclude that the type of mesophase is apparently not influenced by the number of possible hydrogen bonds, which varied with the nature of the linkage groups (amide, ester, urea, urethane), but only by the number of substituents. Likewise, variation of the linkage

Table 5 Transition temperatures ΔC_p values and ΔH values of linear and cyclic oligoethyleneaminoether derivatives **8–14** and the cyclen derivative **15**; T_g glass transition temperature; K, crystalline phases; M, mesophase; I, isotropic phase

		transition temp/°C (ΔH/kJ mol^{-1})										
compound	T_g/°C (ΔC_p/kJ mol^{-1} K^{-1})	K_1		K_2		K_3		K_4		M		I
8	—					•	52.5[a] (4.5)	•	115.0 (68.5)			•
9	—					•	111.0 (57.5)	•	128.0 (45.4)			•
10	—			•	20.0 (46.8)	•	47.5 (33.7)	•	101 (61.5)			•
11	—							•	98.0 (60.6)			•
12	—	•	13.5[b] (15.7)	•	49.5[a] (20.8)	•	68.5[a] (1.4)	•	80.5[a] (55.1)			•
13	—			•	80.0 (3.6)	•	97.0[a] (25.9)	•	124.0 (73.8)			•
14	33[c] (0.03)					•	59.5[b] (5.8)	•	64.9[a] (45.6)	•	67.0 (3.3)	•
15[d]	—							•	108	•	154	•

[a]Only on first heating. [b]On second and further heatings. [c]Determined only on fast heating with 15 K min^{-1} without preceeding recrystallization. [d]Ref. 12.

groups does not influence to a larger extent the lattice spacings in the different mesophase types.

A smectic A phase is verified when only three apolar 'two chain' substituents occupy a space, which would be too small to surround entirely the polar part of the molecule, leading then to a lamellar structure. Two possible lamellar arrangements of **1** and **4**, assumed also for **3** as can be deduced from polarizing microscopy, are shown schematically in Fig. 1.

A minimum number of four 'two chain' groups is necessary for the formation of a hexagonal columnar mesophase ($\mathrm{Col_h}$) in linear oligoethyleneamine derivatives **2**, **5**, **6** and **7**, as well as in the cyclic derivative **15**.

(vi) Contrary to the influence on the melting temperature of the linear derivatives, changing from amide to urea groups (comparing **2** with **6**) increases the clearing temperature of the $\mathrm{Col_h}$ phase. The highest T_c is found in compound **7** with urea/urethane linking groups.

(vii) With respect to the linear derivatives with three substituents, the mesomorphism of the cyclic compound **14** apparently plays an intermediate role between the lamellar and columnar state, resulting in a cubic phase. Such cubic phases likewise exist with other members of oligoethyleneamine derivatives, *i.e.* linear 2,2-tri[15] and 2,2,2-tet[16] derivatives.

The discussion[12,13] of two possible mechanisms for the formation of columnar structures of low molecular, linear N-acylated oligoamine **2** involves the formation of columnar aggregates by intramolecular or intermolecular hydrogen bonds. The meaning is that a 'discoid geometry could perhaps be achieved by means of intramolecular hydrogen bonding between terminal amide groups', leading to a 'stacking of these cyclic subunits into a columnar arrangement. Alternatively, the formation of intermolecular hydrogen bonds between' the terminal amide groups of 'the oligomeric subunits' was 'considered: the column would then be formed by a helically folded chain of hydrogen-bonded oligoamide molecules'.

The existence of a hexagonal columnar ($\mathrm{Col_h}$) mesophase in compound **5**, which in contrast to **2** does not possess the possibility of forming hydrogen bonds, demonstrates that neither a ring closure *via* intramolecular hydrogen bonding and thus the formation of a disc-like structure nor a helix formation *via* intermolecular hydrogen bonding is essential for the formation of a columnar arrangement.

In other words, neither a role as 'molecular mesogens', in terms of classical molecular anisometry, nor a role as 'supramolecular mesogens' *via* hydrogen bonding is responsible for the observed liquid crystallinity.

What then would be the driving force for the mesomorphism in this class of compounds? We conclude that microphase separation of polar and apolar parts plays the dominant role. With four substituents in **2**, **5**, **6** and **7**, the apolar parts of the molecule fill the space around the polar backbone, leading thus to the columnar arrangement. The column core is formed by the backbone of the oligoethyleneamine derivative. Without the above discussed role of hydrogen bonds and with respect to the conformational flexibility of the ethylene bridges, instead of a regular helix a more or less irregular twisting of the backbone of the polar core, radially surrounded by the apolar alkyl sidechains (Fig. 2), would then be the third alternative to the models discussed above for **2**.[12,13]

Due to its conformational flexibility, the cyclic derivative **15** with four 'two chain' substituents is likewise assumed to fill up the inner volume of a column, not in the conventional 'discotic' manner, but in a more or less flexible fashion with its microphase-separated polar and apolar parts.

With respect to the formation of hexagonal columnar phases of N-acylated linear poly(ethyleneimine)s or substituted poly(oxazoline)s,[17] two models have been discussed.[13] In the first model, the column core is described as being formed by a single polymer chain with a helical conformation, while in the second model it is formed by several polymer chains, more or less stretched along the central core axis. The first model (helix model) is favoured over the second one.[13] Because of the absence of hydrogen bonding, not only in **5** but also along the backbone of the 'two chain' substituted poly(ethyleneimine)s, and with respect to the flexibility of the ethylene bridges in the backbone, again the microphase separation or core/shell structure of a column with polar core and apolar shell should be taken into account as a third alternative to the two models discussed above for the 'two chain' substituted poly(ethyleneimine)s.[13] This possibility would also explain very simply that, with the same backbone, the related N-benzoyl

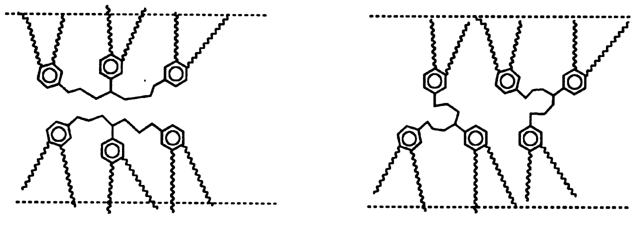

Fig. 1 Possible schematic arrangements of linear oligoethyleneamine derivatives with three 'two chain' substituents to give lamellar structures

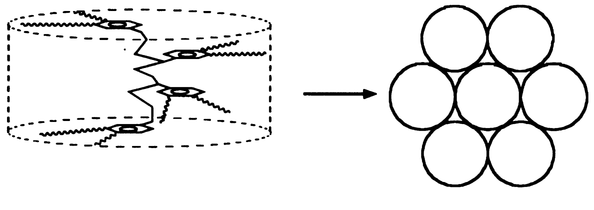

Fig. 2 Schematic arrangement of linear oligoethyleneamine derivatives with a minimum number of four 'two chain' substituents to give the polar core and apolar shell of a column in a hexagonal array

substituted poly(ethyleneimine) exhibits a lamellar crystalline structure.[27] In this case, the absence of alkyl chains is apparently mainly responsible for the lamellar morphology: the interface curvature between two separated phases depends, among other factors, on the space required of one of the phases.[28] This is also valid for such different cases as micellar systems[29] or block copolymers.[30] In the field of liquid crystallinity this point of view plays a role in amphiphilic mesogens,[31] or in compounds which contain a polar macrocyclic core and 'wedge'- or 'V'-shaped apolar groups, filling the space in the outer sphere of a columnar arrangment.[32,33] Likewise in 'tubular' architectures with 'taper shaped' sidegroups, the columnar core/shell structure ('*endo*/*exo*' structure) is caused by the 'microsegregation of polar groups' [*e.g.* flexible oligooxyethylene segments, poly(methacrylate) backbones] 'from the nonpolar aliphatic and aromatic groups at the column periphery'.[34]

Of course, if other interactions like supramolecular (hydrogen bonding, ionic or charge transfer forces) or sterical forces (*e.g.* incorporation of classical anisometric molecular units) are additionally present, they contribute in a specific weighting to the morphological structures observed.

The different requirements for the formation of columnar mesophases, described hitherto in the literature, are (i) classical, more or less stiff, disc-like (discoid) molecular structures ('discotic phases'), (ii) supramolecular arrangements (self-assembling) of single molecules (without classical discoid anisometry) to columnar aggregates *via* hydrogen bonding, ionic forces, charge transfer or because of sterical reasons, (iii) microphase separation of incompatible parts, assumed to play a role also in the mesomorphism of poly(organophosphazene)s[35,36] and perhaps in poly(dialkylsiloxane)s,[37,38] and (iv) regular helical arrangements of stiff polymeric backbones.[39–42] Taking these into account, it is obvious that the denomination 'discotic' (D_h *etc.*) for columnar phases in general is no longer meaningful, or in other words 'the terms disc to describe slices through the column and discotic, to describe the mesophase type, become meaningless expressions'.[33]

Futhermore, it is clear that a number of other denominations, such as *e.g.* pyramidal, bowl-like, phasmidic, tubular, and abbreviations, like ϕ_h (which denotes originally only phasmidic phases after the initial of the greek root φασμα[43]), O_h, B_h, H_I or H_{CI}, are used in the literature by different authors for different columnar phases of one and the same type with respect to X-ray findings.

To avoid this somewhat confusing situation, we[16] and others[44,45] began to use the abbreviations Col_h, for the general 'liquid-crystallographic' relevant term hexagonal columnar mesophase, or Col_r, for rectangular columnar phases *etc.*, taking into account only the X-ray characteristics, independent of a specific molecular structure and the different mechanisms of formation.

Experimental

Instruments

IR: BioRad/Digilab FTS 40. NMR: Bruker AC 250, 250 MHz. MS: Varian 312. SEC (size exclusion chromatography, GPC): Waters ALC 200, RI-Detector Melz LCD 201, eluent THF, elution rate 0.5 ml/min^{-1}; 2×60 cm PL columns, 5 μm particle size, 100 and 500 Å pore width. Elemental analysis: Mikroanalytisches Labor Ilse Beetz, Kronach. Polarizing microscope: Leitz Laboluz 12 pol, hot stage Mettler FP 82, control unit Mettler FP80, photoautomat Wild MPS 45/51 S; DSC: Perkin-Elmer DSC 7, standard heating rate 10 K min^{-1}. X-Ray measurements were performed with a WAXS-Goniometer Siemens D 5000, $\theta/2\theta$, Cu-Kα: 1.5418 Å, in the mesophase, after cooling from the isotropic phase.

Materials

Argon was dried over molecular sieves and potassium on aluminum oxide. Dioxane was refluxed over potassium and distilled under inert gas. The relevant oligoethylene-amines and -amino ethers are commercially available in high purity grade.

Synthesis

The purity of all new compounds was checked by IR, ^{1}H NMR, ^{13}C NMR and mass spectroscopy, SEC (size exclusion chromatography, GPC) and partially by elemental analysis. Yields, MS data and the elution volume of the obtained SEC single peaks are given in Table 6. 3,4-Bis(decyloxy)benzoyl chloride was synthesized using previously described methods.[46] 3,4-Bis(decyloxy)phenyl isocyanate was obtained in high yield from 3,4-bis(decyloxy)benzoic acid by standard reaction with the corresponding azide,[47] which was obtained in high purity after precipitation from toluene solution in the freezer, filtration and subsequent column chromatography on silica gel with toluene. The subsequent Curtius rearrangement[47] yielded, after 3 h and evaporation of toluene, the pure isocyanate, which was stored under inert gas.

Ester endgroup derivatives. The acylation of compounds **3**, **4** and **5** was performed using the method for the synthesis of related amindes,[15] with a reaction time of 12 h instead of 8 h, at 80 °C.

Compound **3**: ν(KBr)/cm^{-1} 3364, 2956, 2924, 2854, 1717, 1632, 1600, 1583, 1510, 1467, 1431, 1272, 1224, 1139, 762; δ_H(CDCl$_3$) 7.55 (d, 2H, aromatic), 7.45 (d, 1H, aromatic), 7.30 (br m, 2H, aromatic, NH), 6.65–6.85 (m, 5H, aromatic), 4.40 (br t, 2H, CO_2CH_2), 3.60–4.10 (m, 18H, OCH_2, CH_2N), 1.8 (m, 12H, OCH_2CH_2), 1.1–1.6 (m, 84H, CH_2), 0.85 (t, 18H, CH_3); δ_C(CDCl$_3$), 173.7 (NCO), 167.3 (NHCO), 166.0 (CO_2), 153.5, 151.6, 150.2, 149.1, 148.7, 148.6, 128.0, 126.4, 123.6, 121.6, 119.6, 119.5, 114.1, 112.9, 112.5, 112.2, 111.8 (aromatic), 69.2, 69.1, 69.0 (OCH_2), 61.9 (CO_2CH_2), 48.0, 44.7, 39.1 (CH_2N), 31.9–22.4 (CH_2), 14.0 (CH_3) (Calc. for $C_{85}H_{144}N_2O_{10}$: C, 75.40; H, 10.72; N, 2.07. Found: C, 75.79; H, 10.73; N 2.14%).

Compound **4**: ν(KBr)/cm^{-1} 2956, 2924, 2855, 1714, 1635, 1600, 1515, 1467, 1431, 1271, 1214, 1139, 1019, 7562; δ_H(CDCl$_3$) 7.65 (d, 2H, aromatic), 7.45 (s, 2H, aromatic), 6.70–6.90 (m, 5H, aromatic), 4.40 (br t, 4H, CO_2CH_2), 3.60–4.10 (m, 16H, OCH_2, CH_2N), 1.8 (m, 12H, OCH_2CH_2), 1.1–1.6 (m, 84H, CH_2), 0.85 (t, 18H, CH_3); δ_C(CDCl$_3$), 173.7 (NCO), 166.1 (CO_2), 153.8, 151.3, 149.1, 148.7, 128.0, 126.4, 123.6, 121.6, 119.6, 114.1, 112.2, 111.8 (aromatic), 69.2, 69.1, 69.0 (OCH_2), 61.9 (CO_2CH_2), 49.0 (CH_2N), 31.9–22.6 (CH_2), 14.1 (CH_3) (Calc. for $C_{85}H_{143}NO_{11}$: C, 75.34; H, 10.64; N, 1.03. Found: C, 75.48; H, 10.52; N, 1.03%).

Compound **5**: ν(KBr)/cm^{-1} identical to that for **4**; δ_H(CDCl$_3$)

Table 6 Yields, mass spectra values and elution volumes (V_e) of size exclusion chromatograms (SEC, GPC) of compounds **3–14**

compound	yield (%)	mass spectrum m/z (intensity, %)	SEC V_e/ml
3	71	1353 ($M^{\bullet +}$, 0.2%), 153 (100%)	25.9
4	29	1354 ($M^{\bullet +}$, 1.8%), 153 (100%)	25.9
5	62	1812 ($M^{\bullet +}$, 0.9%), 153 (100%)	25.9
6	72	151 (100%)	24.6
7	74	151 (100%)	23.7
8	55	936 ($M^{\bullet +}$, 18%), 179 (100%)	25.5
9	59	980 ($M^{\bullet +}$, 18%), 178 (100%)	25.8
10	47	1461 ($M^{\bullet +}$. 0.3%)	24.8
11	29	151 (100%)	25.3
12	41	982 ($M^{\bullet +}$, 1.8%), 417 (100%)	25.6
13	23	151 (100%)	25.5
14	58	1422 ($M^{\bullet +}$, 0.2%), 43 (100%)	24.7

7.65 (d, 2H, aromatic), 7.45 (s, 2H, aromatic), 6.70–6.90 (m, 8H, aromatic), 4.40 (br t, 4H, CO_2CH_2), 3.60–4.10 (m, 24H, OCH_2, CH_2N), 1.8 (m, 16H, OCH_2CH_2), 1.1–1.6 (m, 112H, CH_2), 0.85 (t, 24H, CH_3); $\delta_C(CDCl_3)$, 173.4 (NCO), 166.2 (CO_2), 154.2, 151.8, 149.5, 148.9, 128.1, 126.4, 123.3, 121.8, 119.9, 113.8, 112.0, 111.8 (aromatic), 69.3, 69.1, 69.0 (OCH_2), 61.7 (CO_2CH_2), 49.1 (CH_2N), 31.9–22.6 (CH_2), 14.0 (CH_3) (Calc. for $C_{114}H_{192}N_2O_{14}$: C, 75.45; H, 10.66; N, 1.54. Found: C, 75.58; H, 10.66; N, 1.50%).

Derivatives with urea and urethane substituents. For compounds **6** and **7**, 1 mmol of the relevant amine or the compound with terminal hydroxy groups was added under inert gas to 3,4-bis(decyloxy)phenyl isocyanate (4.4 mmol) in 80 ml dry dioxane and stirred 6 h at 80 °C. The conversion was followed by the decrease of the isocyanate peak in the IR spectrum of samples taken from the reaction mixture under inert gas at different times. At the end of the reaction, the solvent was evaporated and the white residue recrystallized from ethyl acetate, followed by a column chromatography on silica gel 60 with ethyl acetate and a second recrystallization from hexane–ethyl acetate–ethanol (6:3:1). Finally, the products were lyophilized from benzene solution.

Compound **6**: $\nu(KBr)/cm^{-1}$ 3308, 3142, 2956, 2924, 2855, 1714, 1647, 1608, 1556, 1515, 1469, 1426, 1263, 1228, 1134, 1019, 802, 722; $\delta_H(CDCl_3)$ 8.5–8.6 (br s, 2H, NH), 6.9–7.3 (m, 8H, aromatic, NH), 6.5–6.8 (m, 6H, aromatic), 5.6–5.8 (br t, 2H, NH), 3.7–4.0 (m, 16H, OCH_2), 3.1–3.5 (br m, 12H, CH_2N), 1.8 (m, 16H, OCH_2CH_2), 1.1–1.6 (m, 112H, CH_2), 0.85 (t, 24H, CH_3); $\delta_C(CHCl_3)$, 157.1 (NHCON), 156.7 (NHCONH), 149.6, 149.4, 145.1, 144.7, 133.6, 132.8, 132.6, 114.9, 114.8, 112.1, 111.9, 106.9 (aromatic), 70.0, 69.1, 69.0 (OCH_2), 49.6, 48.0, 47.3, 39.5 (CH_2N), 31.9–22.7 (CH_2), 14.1 (CH_3) (Calc. for $C_{114}H_{198}N_8O_{112}$: C, 73.11; H, 10.66; N, 5.98. Found: C, 73.39; H, 10.26; N, 5.59%).

Compound **7**: $\nu(KBr)/cm^{-1}$ 3316, 3143, 2954, 2926, 2855, 1710, 1651, 1606, 1592, 1518, 1467, 1431, 1259, 1226, 1134, 1019, 799, 722; $\delta_H(CDCl_3)$ 7.8–8.0 (br s, 2H, NH), 7.3 (d, 2H, aromatic), 7.0–7.1 (br s, 2H, NH), 6.9 (dd, 2H, aromatic), 6.6–6.8 (m, 8H, aromatic), 4.4 (br m, 4H, CO_2CH_2), 3.8–4.0 (m, 16H, OCH_2), 3.4–3.7 (br m, 8H, CH_2N), 1.8 (m, 16H, OCH_2CH_2), 1.1–1.6 (m, 112H, CH_2), 0.85 (t, 24H, CH_3); $\delta_C(CDCl_3)$, 155.8 (NHCON), 154.0 ($NHCO_2$), 149.7, 149.6, 145.6, 144.8, 133.4, 131.2, 114.9, 114.7, 111.7, 111.2, 106.8, 106.0 (aromatic), 70.1, 69.9, 69.1, 69.0 (OCH_2), 63.2 (CO_2CH_2), 47.7 (CH_2N), 31.9–22.7 (CH_2), 14.1 (CH_3) (Calc. for $C_{114}H_{196}N_6O_{14}$: C, 73.03; H, 10.54; N, 4.48. Found: C, 73.58; H, 10.67; N, 4.79%).

Derivatives with oxobridges. The acylation of compounds **8**–**10**, **12** and **14** was performed using the method for synthesis of related amides,[15] while compounds **11** and **13** were synthesized using 3,4-bis(decyloxy)phenyl isocyanate (2.2 mmol) following the procedure for **6** and **7**.

Compound **8**: $\nu(KBr)/cm^{-1}$ 3291, 2956, 2923, 2852, 1633, 1602, 1583, 1542, 1514, 1468, 1317, 1273, 1225, 1135, 1067, 763, 720; $\delta_H(CDCl_3)$ 7.4 (d, 2H, aromatic), 7.2 (dd, 2H, aromatic), 6.75 (d, 2H, aromatic), 6.4–6.6 (br t, 2H, NH), 4.0 (t, 8H, OCH_2), 3.5–3.8 (br m, 8H, OCH_2CH_2N), 1.8 (m, 8H, OCH_2CH_2), 1.1–1.6 (m, 56, CH_2), 0.85 (t, 12H, CH_3) $\delta_C(CDCl_3)$, 167.4 (NHCO), 151.7, 148.7, 126.6, 119.6, 112.7, 112.0 (aromatic), 69.5, 69.1, 68.9 (OCH_2), 39.6 (NCH_2), 31.8–22.6 (CH_2), 14.0 (CH_3).

Compound **9**: $\nu(KBr)/cm^{-1}$ identical to that for **8**; $\delta_H(CDCl_3)$ 7.4 (d, 2H, aromatic), 7.2 (dd, 2H, aromatic), 6.8 (d, 2H, aromatic), 6.5–6.6 (br t, 2 H, NH), 4.0 (m, 8H, OCH_2), 3.5–3.8 (br m, 12H, OCH_2CH_2N), 1.8 (m, 8H, OCH_2CH_2), 1.1–1.6 (m, 56H, CH_2), 0.85 (t, 12H, CH_3); $\delta_C(CDCl_3)$, 167.1 (NHCO), 151.9, 148.9, 126.8, 119.4, 112.9, 112.1 (aromatic), 70.2, 69.9, 69.3, 69.0 (OCH_2), 39.7 (NCH_2), 31.8–22.6 (CH_2), 14.0 (CH_3).

Compound **10**: $\nu(KBr)/cm^{-1}$ identical to that for **8**; $\delta_H(CDCl_3)$ 7.0 (s, 4H, aromatic), 6.5–6.6 (br t, 2H, NH), 4.0 (m, 12H, OCH_2), 3.6 (m, 12H, OCH_2CH_2O, OCH_2CH_2N), 1.8 (m, 12H, OCH_2CH_2), 1.1–1.6 (m, 84H, CH_2), 0.85 (t, 18H, CH_3); $\delta_C(CDCl_3)$, 167.3 (NHCO), 153.0, 141.2, 129.3, 119.4, 105.8 (aromatic), 73.4, 69.8, 69.3, (OCH_2), 39.8 (NCH_2), 31.9–22.6 (CH_2), 14.0 (CH_3).

Compound **11**: $\nu(KBr)/cm^{-1}$ 3314, 3142, 2956, 2923, 2852, 1643, 1602, 1583, 1542, 1514, 1468, 1317, 1273, 1225, 1135, 1067, 763, 720; $\delta_H(CDCl_3)$ 7.4 (s, 2H, NH), 7.1 (d, 2H, aromatic), 6.6–6.8 (d, 2H, dd, 2H, aromatic), 5.5 (t, 2H, NH), 3.9 (t, 8H, OCH_2), 3.5–3.7 (br m, 8H, OCH_2CH_2N), 3.3–3.4 (m, 4H, $CONHCH_2$), 1.80 (m, 8H, OCH_2CH_2), 1.10–1.60 (m, 56H, CH_2), 0.85 (t, 12H, CH_3); $\delta_C(CDCl_3)$, 156.9 (NHCONH), 149.6, 144.9, 132.9, 115.0, 112.3, 107.2, (aromatic), 70.5, 70.2, 70.0, 69.0 (OCH_2), 40.1 (NCH_2), 31.9–22.6 (CH_2), 14.0 (CH_3).

Compound **12**: $\nu(KBr)/cm^{-1}$ 2956, 2924, 2855, 1635, 1600, 1582, 1515, 1467, 1431, 1271, 1214, 1139, 1019, 762; $\delta_H(CDCl_3)$ 7.0–7.3 (m, 4H, aromatic), 6.8 (d, 2H, aromatic), 3.4–4.1 (m, 24H, OCH_2, OCH_2CH_2N), 1.80 (m, 8H, OCH_2CH_2), 1.10–1.60 (m, 56H, CH_2), 0.85 (t, 12H, CH_3); $\delta_C(CDCl_3)$, 172.4 (NCO), 150.2, 148.6, 128.5, 120.9, 113.4, 112.7 (aromatic), 69.1 (OCH_2), 52.2 (OCH_2CH_2N), 48.4 (NCH_2), 31.9–22.6 (CH_2), 14.1 (CH_3) (Calc. for $C_{60}H_{106}N_2O_8$: C, 73.27; H, 10.86; N, 2.85. Found: C, 73.77; H, 10.58; N, 2.86%).

Compound **13**: $\nu(KBr)/cm^{-1}$ 3311, 3140, 2954, 2922, 2854, 1646, 1602, 1586, 1542, 1514, 1464, 1321, 1274, 1225, 1139, 1067, 761, 722; $\delta_H(CDCl_3)$ 7.6 (s, 2H, NH), 7.15 (d, 2H, aromatic), 6.75 (d, 2H, aromatic), 6.55 (dd, 2H, aromatic), 3.7–4.1 (m, 16H, OCH_2, OCH_2CH_2N), 3.3–3.6 (br m, 8H, CH_2N), 1.80 (m, 8H, OCH_2CH_2), 1.10–1.60 (m, 56H, CH_2), 0.85 (t, 12H, CH_3); $\delta_C(CDCl_3)$, 156.7 (NHCON), 149.9, 144.5, 133.7, 115.6, 110.6, 106.1 (aromatic), 70.3, 69.8, 69.0 (OCH_2, OCH_2CH_2N), 52.2 (NCH_2), 31.6–22.6 (CH_2), 14.0 (CH_3).

Compound **14**: $\nu(KBr)/cm^{-1}$ identical to that for **12**; $\delta_H(CDCl_3)$ 6.6–7.1 (br m, 9H, aromatic), 3.4–4.1 (br m, 28H, OCH_2, OCH_2, CH_2N), 1.80 (m, 12H, OCH_2CH_2), 1.10–1.60 (m, 84H, CH_2), 0.85 (t, 18H, CH_3); $\delta_C(CDCl_3)$ 172.1 (NCO), 150.2, 149.1, 148.8, 128.6, 128.2, 119.3, 118.9, 112.9, 112.5, 112.2, 112.0 (aromatic), 69.8, 69.1 (OCH_2), 52.5 (OCH_2CH_2N), 49.7, 47.8, 42.9 (NCH_2), 31.8–22.6 (CH_2), 14.0 (CH_3) (Calc. for $C_{89}H_{151}N_3O_{10}$: C, 75.11; H, 10.69; N, 2.95. Found: C, 75.04; H, 10.90; N, 3.00%).

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