139. Structural Isomerism in Polycondensates

Part IV[1])

Synthesis and Characterization of Liquid Crystalline Poly(azomethines) and Low Molecular Weight Model Compounds

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With the aim to investigate the influence of structural isomerism on the mesomorphic thermal stability in main chain thermotropic polycondensates, a series of poly(azomethines) and low molecular weight models have been prepared. The model compounds exhibit smectic and/or nematic mesophases whose stabilites are very sensitive to structural modifications. On the basis of the above results, monomers **2**, **5**, **6**, **8**, **9**, **23**, **25**, and **26** were selected to synthesize oligomers **27**–**33**. The oligomer **33** obtained from the nonsymmetric diamine **23** has a lower melting point than the symmetric oligomer **28**, but a similar liquid crystalline range.

Introduction. – Recently, we have shown that the synthesis of polycondensates with a predetermined degree of structural order is achievable in one step from a nonsymmetrical monomer (XabX) and a symmetrical one (HccH). Structurally ordered polyureas [1] and polyamides [2] were prepared as well as some analogous structurally disordered polymers [3].

Among the possible applications of these results, the influence of structural order on the existence of mesomorphic phases in main chain thermotropic polymers seems particularly interesting. Different types of main chain thermotropic polymers are described in the literature [4]. For our scope, poly(azomethines) appear to be suitable for the following reasons: *i*) nonsymmetric diamines XabX ($X=NH_2$), in which the NH_2 groups have largely different reactivity, can be easily synthesized; *ii*) the polycondensation between diamines and dialdehydes has already been studied [5], and *iii*) the polymers have a reasonable thermal stability [6]. To identify structures having a sufficient solubility coupled with a relatively low melting point, a number of model compounds have been first prepared, and their anisotropic liquid phases were investigated. On the basis of their properties, low molecular weight poly(azomethines) have been synthesized using symmetric and nonsymmetric monomers.

Results and Discussion. – A. *Model Compounds.* The diamines **1**–**9** were first condensed with either the 4-pentoxybenzaldehyde (**10**) or the 4-pentoxyacetophenone (**11**) for preparing the symmetrical compounds **12**–**22**. Their transition temperatures and entropy changes associated with the melting and clearing points are collected in *Table 1.*

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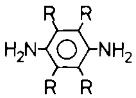
[1]) Part III: [1].



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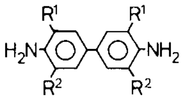

3 $R^1 = R^2 = H$
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8 $R^1 = H$, $R^2 = CH_3$
9 $R^1 = R^2 = CH_3$

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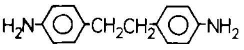

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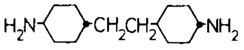

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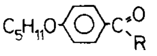

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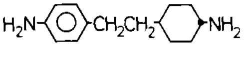

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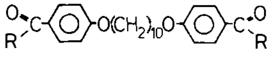

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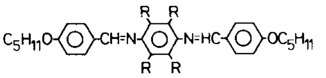
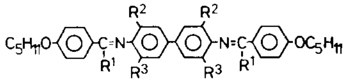
26 R = CH_3

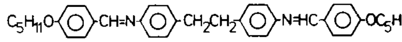


12 R = H
13 R = CH_3



14 $R^1 = R^2 = R^3 = H$
18 $R^1 = R^2 = H$, $R^3 = OCH_3$
19 $R^1 = R^2 = H$, $R^3 = CH_3$
20 $R^1 = H$, $R^2 = R^3 = CH_3$
21 $R^1 = CH_3$, $R^2 = R^3 = H$
22 $R^1 = R^2 = CH_3$, $R^3 = H$

15



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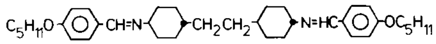

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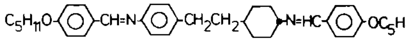


24

These compounds will be discussed following the increasing complexity of their mesogenic unit.

Compound **12** having a 1,4-phenylene unit in its rigid segment shows a smectic mesophase and a nematic one, while the tetramethyl-substituted **13** exhibits only a nematic mesophase. The benzidine derivative **14** presents a smectic mesophase and a nematic one. In **15** replacement of the benzidine moiety by two *trans*-cyclohexyl units lowers both the melting and clearing points of 107° and 65°, respectively. The presence of an ethylene fragment in the central core also depresses $T_{n,i}$ as shown by **16** and **17**.

This result could be due to an increase of the flexibility of the mesogenic unit. Substitution of one *ortho*-position next to the N-atom not only causes a decrease of the clearing temperature as illustrated by **18** and **19**, but also eliminates the smectic mesophases. This behavior has been observed for other systems and has been attributed to a decrease of the intermolecular attractive forces [8]. In contrast to the large nematic range exhibited by **18** and **19** (126° and 144°, resp.), a remarkable contraction of the anisotropic region occurs for **20** in which both *ortho*-positions with respect to each N-atom are occupied by a Me group. In compounds **21** and **22** Me substitution at the C-atom of the azomethine function also suppresses the smectic mesophases.

Table 1. *Phase-Transition Temperatures*a)b) *and Entropy Changes Associated with the Melting and Clearing Points of the Bis(azomethines)*

Model Compound	$T_{c,s}$ [°C]	$\Delta S_{c,s}$ [e.u.]	$T_{c,n}$ [°C]	$\Delta S_{c,n}$ [e.u.]	$T_{s,s}$ [°C]	$T_{s,n}$ [°C]	$T_{n,i}$ [°C]	$\Delta S_{n,i}$ [e.u.]	$\Delta T_{c,i}$ [°C]
12	(169)d)	11.85				172	265	1.09	96
	(171)d) [13]					172 [13]	264 [13]		
13			162 (152)	21.13			197	1.78	35
14c)	243 (223)	12.41				303	390	1.22	147
	244 [14]					303 [14]	393 [14]		
15c)	136 (89)	14.36				225	325	1.25	189
16	143 (125)	13.43				205	285	3.07	142
17	143 (103)	10.86			165	193	265	1.96	122
18			118 (87)	28.26			244	1.21	126
19			151 (98)	20.91			295	1.23	144
20			206 (177)	19.54			211	1.86	5
21			229 (212)	23.40			315	2.50	86
22			145 (113)	29.28			233	1.98	88
24c)	100 (45)	15.77				163	268	2.67	168

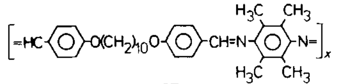
a) Transitions: c,s = crystal-to-smectic, c,n = crystal-to-nematic, s,s = smectic-to-smectic, s,n = smectic-to-nematic, n,i = nematic-to-isotropic; $\Delta T_{c,i}$ = liquid crystalline range.

b) The values between parentheses correspond to the transition temperatures obtained on cooling.

c) Nematic droplets [7] were observed by polarized microscopy.

d) Transition from monotropic smectic.

To investigate the possible influence of the lack of symmetry in a bis(azomethine) on the liquid crystal transition temperatures, **23** was reacted with **10** to give the model compound **24**. A comparison of the entropy changes of **24** ($\Delta S_{c,s}$ 15.77 e.u.; $\Delta S_{n,i}$ 2.67 e.u.) with those of the symmetric models **16** ($\Delta S_{c,s}$ 13.43 e.u.; $\Delta S_{n,i}$ 3.07 e.u.) and **17** ($\Delta S_{c,s}$ 10.86 e.u.; $\Delta S_{n,i}$ 1.96 e.u.) indicates that **24** displays a nematic mesophase lacking head-to-head and tail-to-tail ordering of the nonsymmetric molecules within the nematic regions. Moreover, $T_{c,s}$ and $T_{s,n}$ of **24** are much lower than those of **16** and **17**, while their $T_{n,i}$ are similar. As a consequence, **24** exhibits a wider liquid crystalline range than both **16** and **17**.



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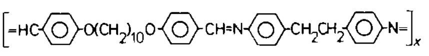

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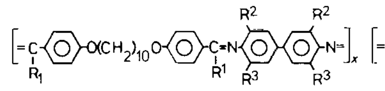
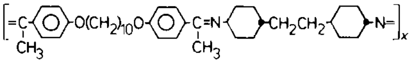


29 $R^1 = R^2 = H$, $R^3 = CH_3$ **31** $R^1 = R^2 = CH_3$, $R^3 = H$
30 $R^1 = H$, $R^2 = R^3 = CH_3$



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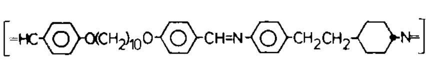

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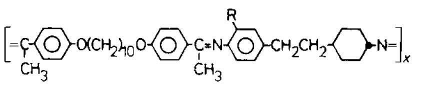

34 R = H
35 R = CH_3

B. *Oligomers*. By reacting either **25** or **26** with **2**, **5**, **6**, and **8** following the procedure used for the model compounds, oligomers **27**–**32** were synthesized. Oligomers **27**, **30** and **32** are soluble in $CHCl_3$, and their molecular weights could be measured by vapor-pressure osmometry. Compounds **28**, **29**, and **31** are insoluble in common organic solvents and dissolve only in protic media such as H_2SO_4 and *m*-chlorophenol. No molecular peak was observed by means of high resolution mass spectrometry, and their molecular weights could not be determined so far. As in some cases the mesophases of the oligomers have not been identified, the term liquid-crystal-to-liquid-crystal transition (abbreviated to $T_{lc,lc}$) will be used to mention a phase transition within the liquid crystalline region. However, in compounds **29**, **32**, and **33**, the observation of nematic droplets allowed an unambiguous identification of the mesophase textures.

Table 2. *Phase-Transition Temperatures*[a])[b]) *and Molecular Weights*[c]) *of the Oligomeric Azomethines*

Oligomer	$\bar{M}_n$	$\overline{DP}$[d])	T_m [°C]	$T_{lc,lc}$ [°C]	T_c [°C]	$\Delta T_{c,i}$ [°C]
27	1250	5	228 (165)	–	263	35
28	–	–	200 (182)	293	352	152
29[e])	–	–	224 (175)	–	385	161
30	3500	12	280 (268)	–	–	–
31	–	–	200 (153)	–	260	60
32[e])	1540	5	194 (185)	–	220	26
33[e])	–	–	183 (161)	280	315	132

[a]) T_m = melting point, $T_{lc,lc}$ = liquid-crystal-to-liquid-crystal transition, T_c = clearing point, $\Delta T_{c,i}$ = liquid crystalline range.

[b]) The values between parentheses correspond to the transition temperatures obtained on cooling.

[c]) By vapor-pressure osmometry in $CHCl_3$ at 25°.

[d]) Polycondensation degree calculated from $\bar{M}_n$ regardless the end groups.

[e]) Nematic droplets [7] were obtained by polarized microscopy.

Oligomer **27** shows only one, the nonsubstituted **28** two, and the substituted compounds **29**–**32** only one mesophase. The comparison of **28** with **32** as well as the data of the models **16** and **17** indicate that the replacement of the methin H-atom by a CH_3 group causes a reduction of the liquid crystalline range ($\Delta T_{c,i}$). This is also confirmed by comparing **29** with **31**. The results of **29** and **30**, the latter exhibiting no anisotropic behavior, indicate that $\Delta T_{c,i}$ is very sensitive to substitution in *ortho*-position with respect to the N-atom. This is in agreement with the indications given by the models **19** and **20**.

Under the same reaction conditions as used for preparing oligomers **27**–**32**, the nonsymmetrical diamine **23** was condensed with **25** to give **33**. Under these conditions, no substantial structural order should be expected in **33**. *Table 2* shows a depression of T_m (17°), of $T_{lc,lc}$ (13°), and of T_c (37°) for **33** with respect to the symmetrical compound **28**. Thus, the oligomers exhibit a smaller difference between their melting points than the models **16** or **17** with respect to **24**. This fact could be ascribed to a different degree of polymerization between **28** and **33**. The $\Delta T_{c,i}$ of **33** is smaller than the one of **28**. This is rather unexpected according to the indications obtained from the model compounds **16**, **17**, and **24**. It might also be connected to either a different degree of polymerization or to the existence of a small degree of structural order in **33**.

Conclusion. – The research on low molecular weight models described in the first part of this paper has shown that structures like **24** exhibit a low melting point and a high mesomorphic thermal stability. The polymers reflect part of the properties of the model compounds, the major problem beeing their poor solubility in common aprotic solvents. Because of the large prevalence of the (*E*)-configuration of the C=N function [9], no problem should be encountered due to the possible (*E*/*Z*) isomerism. The most interesting repeating units from the viewpoint of the solubility of the corresponding polymers seem to be **34** and **35**. Work is in progress to synthesize polycondensates with these structures and with different degree of structural regularity.

Both, the investigation on the model compounds and oligomers confirmed the tendency of bis(azomethines) containing benzene and 1,4-*trans*-cyclohexane rings to form mesophases whose properties and thermal stability are markedly sensitive to structural modifications.

Experimental Part

General. The starting materials phenylene-1,4-diamine (**1**; m.p. 143.5°), 2,3,5,6-tetramethylphenylene-1,4-diamine (**2**; m.p. 152.3°), biphenyl-4,4′-diamine (**3**; m.p. 124.7°), 4,4′-ethylenedi(phenylamine) (**5**; m.p. 137.6°), 3,3′-dimethoxybiphenyl-4,4′-diamine (**7**; m.p. 136.4°), 3,3′-dimethylbiphenyl-4,4′diamine (**8**; m.p. 128.2°), and 3,3′,5,5′-tetramethylbiphenyl-4,4′-diamine (**9**; m.p. 167.8°) were purchased from *Fluka* and sublimed before use. The 4,4′-(decamethylenedioxy)dibenzaldehyde [10] (**25**; m.p. 73.5°; [8]: m.p. 78–80°), 4-pentoxybenzaldehyde [11] (**10**; b.p. 115–117°/1 Torr; [11]: b.p. 156–158°/10 Torr) and 4-pentoxyacetophenone [12] (**11**; b.p. 126–128°/1 Torr; [12]: b.p. 181–183°/18 Torr) were prepared according to literature procedures. The synthesis of *trans,trans*-bicyclohexane-4,4′-diamine (**4**), *trans,trans*-4,4′-ethylenedi(cyclohexylamine) (**6**) and 4-(*trans*-4-aminocyclohexyl)aniline (**23**) will be reported elsewhere [15]. Optical studies of the textures were conducted under Ar with a polarizing *Universal R Pol Zeiss* microscope. Transition temp. and m.p. were determined by a differential scanning calorimeter (*Mettler DSC 3000*) at a heating rate of 10° under a flow of N_2. The mol. wt. of the oligomers were determined by vapor-pressure osmometry in $CHCl_3$ at 25° using a *Corona Wescan 232 A* instrument. ^{1}H-NMR (360 MHz): in $CDCl_3$; *Bruker AM 300 WB*; δ in ppm relative to TMS as internal standard, J in Hz.

4,4′-(Decamethylendioxy)di(acetophenone) (**26**) was synthesized analogously to **25** [10] and recrystallized from EtOH. M.p. 109.5°. ^{1}H-NMR: 1.3–1.6 (*m*, 12 H); 1.80 (*m*, J = 6.5, 4 H); 2.55 (*s*, 6 H); 4.01 (*t*, J = 6.5, 4 H); 6.91 (*m*, 4 H); 7.92 (*m*, 4 H). Anal. calc. for $C_{26}H_{34}O_4$ (410.22): C 76.06, H 8.35; found: C 76.23, H 8.44.

N,N′-*Bis(4-pentoxybenzylidene)phenylene-1,4-diamine* (**12**). A soln. of 0.28 g (2.60 mmol) of **1** and 1.00 g (5.20 mmol) of **10** in 20 ml of benzene was heated overnight at reflux temp. The H_2O was continuously eliminated by means of a *Dean-Stark* trap. The mixture was then cooled to r.t. and evaporated. The solids were recrystallized from benzene to afford 1.10 g (93%) of **12**. ^{1}H-NMR: 0.95 (*t*, J = 7.0, 6 H); 1.36–1.50 (*m*, 8 H); 1.77–1.78 (*m*, 4 H); 4.02 (*t*, J = 6.6, 4 H); 6.95–6.99 (*m*, 4 H); 7.24 (*s*, 4 H); 7.82–7.86 (*m*, 4 H); 8.43 (*s*, 2 H). Anal. calc. for $C_{30}H_{36}N_2O_2$ (456.38): C 78.91, H 7.95, N 6.13; found: C 78.78, H 7.98, N 6.17.

Model compounds **13**–**22** and **24** were synthesized according to the above procedure. AcOH (0.5 ml) was added to the reaction mixture for preparing **21** and **22**. The chemical yields ranged from 85 to 90%.

*2,3,5,6-Tetramethyl-*N,N′-*bis(4-pentoxybenzylidene)phenylene-1,4-diamine* (**13**) recrystallized from EtOH. ^{1}H-NMR: 0.95 (*t*, J = 7.1, 6 H); 1.34–1.52 (*m*, 8 H); 1.78–1.87 (*m*, 4 H); 2.07 (*s*, 12 H); 4.03 (*t*, J = 6.6, 4 H); 6.97–7.00 (*m*, 4 H); 7.84–7.87 (*m*, 4 H); 8.08 (*s*, 2 H). Anal. calc. for $C_{34}H_{44}N_2O_2$ (512.32): C 79.65, H 8.65, N 5.46; found: C 79.39, H 8.37, N 5.49.

N,N′-*bis(4-pentoxybenzylidene)biphenyl-4,4′-diamine* (**14**) recrystallized from benzene. ^{1}H-NMR: 0.95 (*t*, J = 7.1, 6 H); 1.39–1.50 (*m*, 8 H); 1.78–1.88 (*m*, 4 H); 4.04 (*t*, J = 6.6, 4 H); 6.97–7.00 (*m*, 4 H); 7.27–7.30 (*m*, 4 H); 7.60–7.66 (*m*, 4 H); 7.84–7.88 (*m*, 4 H); 8.45 (*s*, 2 H). Anal. calc. for $C_{36}H_{40}N_2O_2$ (532.34): C 81.17, H 7.57, N 5.26; found: C 81.41, H 7.83, N 5.23.

trans,trans-N,N′-*Bis(4-pentoxybenzylidene)bicyclohexane-4,4′-diamine* (**15**) recrystallized from EtOH. ^{1}H-NMR: 0.93 (*t*, *J* = 7.1, 6 H); 1.16–1.26 (*m*, 6 H); 1.32–1.47 (*m*, 8 H); 1.49–1.67 (*m*, 4 H); 1.76–1.86 (*m*, 12 H); 3.06–3.13 (*m*, 2 H); 3.98 (*t*, *J* = 6.6, 4 H); 6.88–6.91 (*m*, 4 H); 7.62–7.66 (*m*, 4 H); 8.24 (*s*, 2 H). Anal. calc. for $C_{36}H_{52}N_2O_2$ (544.34): C 79.66, H 9.28, N 5.16; found: C 79.73, H 9.30, N 5.00.

N,N′-*Bis(4-pentoxybenzylidene)-4,4′-ethylenedi(phenylamine)* (**16**) recrystallized from EtOH/benzene 1:1. ^{1}H-NMR: 0.94 (*t*, *J* = 7.1, 6 H); 1.33–1.51 (*m*, 8 H); 1.76–1.86 (*m*, 4 H); 2.94 (*s*, 4 H); 4.01 (*t*, *J* = 6.6, 4 H); 6.94–6.97 (*m*, 4 H); 7.11–7.19 (*m*, 8 H); 7.80–7.84 (*m*, 4 H); 8.38 (*s*, 2 H). Anal. calc. for $C_{38}H_{44}N_2O_2$ (560.36): C 81.44, H 7.85, N 5.00; found: C 81.26, H 7.96, N 4.93.

N,N′-trans,trans-*Bis(4-pentoxybenzylidene)-4,4′-ethylenedi(cyclohexylamine)* (**17**) recrystallized from EtOH/benzene 2:1. ^{1}H-NMR: 0.93 (*t*, *J* = 7.1, 6 H); 1.00–1.07 (*m*, 4 H); 1.21–1.26 (*m*, 6 H); 1.31–1.49 (*m*, 8 H); 1.55–1.86 (*m*, 16 H); 3.06–3.14 (*m*, 2 H); 3.97 (*t*, *J* = 6.6, 4 H); 6.87–6.90 (*m*, 4 H); 7.61–7.66 (*m*, 4 H); 8.24 (*s*, 2 H). Anal. calc. for $C_{38}H_{56}N_2O_2$ (572.36): C 79.95, H 9.53, N 4.91; found: C 79.91, H 9.50, N 4.84.

3,3′-Dimethoxy-N,N′-*bis(4-pentoxybenzylidene)biphenyl-4,4′-diamine* (**18**) recrystallized from EtOH. ^{1}H-NMR: 0.95 (*t*, *J* = 7.1, 6 H); 1.36–1.50 (*m*, 8 H); 1.77–1.87 (*m*, 4 H); 3.97 (*s*, 6 H); 4.03 (*t*, *J* = 6.6, 4 H); 6.95–6.99 (*m*, 4 H); 7.05–7.09 (*m*, 2 H); 7.17–7.24 (*m*, 4 H); 7.86–7.90 (*m*, 4 H); 8.44 (*s*, 2 H). Anal. calc. for $C_{38}H_{44}N_2O_4$ (592.34): C 77.00, H 7.48, N 4.73; found: C 76.74, H 7.46, N 4.75.

*3,3′-Dimethyl-*N,N′-*bis(4-pentoxybenzylidene)biphenyl-4,4′-diamine* (**19**) recrystallized from EtOH. ^{1}H-NMR: 0.95 (*t*, *J* = 7.2, 6 H); 1.34–1.56 (*m*, 8 H); 1.78–1.87 (*m*, 4 H); 2.43 (*s*, 6 H); 4.03 (*t*, *J* = 6.6, 4 H); 6.97–7.00 (*m*, 6 H); 7.43–7.48 (*m*, 4 H); 7.85–7.89 (*m*, 4 H); 8.34 (*s*, 2 H). Anal. calc. for $C_{38}H_{44}N_2O_2$ (560.36): C 81.44, H 7.85, N 5.00; found: C 81.55, H 8.01, N 4.94.

*3,3′,5,5′-Tetramethyl-*N,N′-*bis(4-pentoxybenzylidene)biphenyl-4,4′-diamine* (**20**) recrystallized from EtOH/benzene 5:1. ^{1}H-NMR: 0.95 (*t*, *J* = 7.1, 6 H); 1.34–1.52 (*m*, 8 H); 1.78–1.87 (*m*, 4 H); 2.20 (*s*, 12 H); 4.04 (*t*, *J* = 6.6, 4 H); 6.98–7.01 (*m*, 4 H); 7.30 (*s*, 4 H); 7.83–7.87 (*m*, 4 H); 8.17 (*s*, 2 H). Anal. calc. for $C_{40}H_{48}N_2O_2$ (588.38): C 81.59, H 8.22, N 4.76; found: C 81.37, H 8.29, N 4.68.

N,N′-*Bis(α-methyl-4-pentoxybenzylidene)biphenyl-4,4′-diamine* (**21**) recrystallized from EtOH. ^{1}H-NMR: 0.95 (*t*, *J* = 7.1, 6 H); 1.36–1.49 (*m*, 8 H); 1.77–1.87 (*m*, 4 H); 2.25 (*s*, 6 H); 4.02 (*t*, *J* = 6.6, 4 H); 6.83–6.88 (*m*, 4 H); 6.92–6.97 (*m*, 4 H); 7.58–7.62 (*m*, 4 H); 7.92–7.96 (*m*, 4 H). Anal. calc. for $C_{38}H_{44}N_2O_2$ (560.36): C 81.44, H 7.85, N 5.00; found: C 81.12, H 8.17, N 4.98.

*3,3′-Dimethyl-*N,N′-*bis(α-methyl-4-pentoxybenzylidene)biphenyl-4,4′-diamine* (**22**) recrystallized from EtOH. ^{1}H-NMR: 0.95 (*t*, *J* = 7.0, 6 H); 1.37–1.50 (*m*, 8 H); 1.77–1.87 (*m*, 4 H); 2.15 (*s*, 6 H); 2.18 (*s*, 6 H); 4.03 (*t*, *J* = 6.6, 4 H); 6.68–6.71 (*m*, 27 H); 6.94–6.97 (*m*, 4 H); 7.41–7.46 (*m*, 4 H); 7.96–7.99 (*m*, 4 H). Anal. calc. for $C_{40}H_{48}N_2O_2$ (588.38): C 81.59, H 8.22, N 4.76; found: C 81.46, H 8.44, N 4.78.

N-*(4-Pentoxybenzylidene)-4-{2-[4-((4-pentoxybenzylidene)amino)cyclohexyl]ethyl}aniline* (**24**) recrystallized from EtOH/benzene 2:1. ^{1}H-NMR: 0.93 (*t*, *J* = 6.9, 3 H); 0.95 (*t*, *J* = 7.0, 3 H); 1.04–1.20 (*m*, 2 H); 1.25–1.50 (*m*, 8 H); 1.50–1.70 (*m*, 5 H); 1.70–1.94 (*m*, 8 H); 2.63–2.69 (*m*, 2 H); 3.09–3.16 (*m*, 1 H); 3.98 (*t*, *J* = 6.6, 2 H); 4.02 (*t*, *J* = 6.6, 2 H); 6.88–7.00 (*m*, 4 H); 7.12–7.21 (*m*, 4 H); 7.60–7.66 (*m*, 2 H); 7.80–7.84 (*m*, 2 H); 8.25 (*s*, 1 H); 8.39 (*s*, 1 H). Anal. calc. for $C_{38}H_{50}N_2O_2$ (566.36): C 80.52, H 8.89, N 4.94; found: C 80.47, H 9.11, N 4.91.

Oligomers. They were prepared according to the procedure used for the synthesis of the model compounds. The soluble oligomers **27**, **30**, and **32** were recrystallized from EtOH, benzene/EtOH 10:1, and benzene/EtOH 1:4, resp. The insoluble compounds **28**, **29**, **31**, and **33** were filtered from the reaction mixture, purified by *Soxhlet* extraction for 24 h with EtOH and dried at 60°/10 Torr. Data in *Table 2*. The wide-angle X-ray (WAXS) bands are listed in *Table 3*.

Table 3. *Wide-Angle X-Ray Bands of the Oligomers*[a])

Oligomer	2θ [deg]								
27	11.8,	15.0,	16.6,	17.5,	20.4,	21.3,	23.8,	27.5	
28	23.0,	23.7,	24.5,	26.2,	29.2				
29	14.9,	15.7,	16.8,	18.5,	18.9,	21.2,	23.5,	24.9,	25.7
30	13.1,	16.9,	19.4,	20.0,	22.0,	23.4,	24.0		
31	16.6,	19.3,	20.3,	22.0,	26.0				
32	19.5,	20.6,	22.0,	24.8					
33	22.4,	21.8,	23.5						

[a]) Obtained from powder diagrams at r.t.

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