Liquid Crystalline Azomethines and Polyazomethines Containing Azobenzene and Stilbene Units

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Liquid Crystalline Compounds and Polymers, Azobenzenes with LC-Phases, Stilbenes with LC-Phases, Azomethines with LC-Phases

Azobenzene and stilbene derivatives with azomethine and ester groups and polymers of corresponding structures with mesogens possessing three to four aromatic systems in their mesogenic units have been synthesized, characterized and studied for their liquid crystalline properties by DSC measurements and observation by polarizing microscopy.

Introduction

During our investigations of the properties of liquid crystalline azomethines we synthesized, characterized and investigated some new low molecular weight and polymeric azomethines.

Liquid crystalline azomethines prepared by condensation of 4,4'-diaminoazobenzene and 4,4'-diaminostilbene with β-alkylbenzaldehydes are known since 1911 [1] and 1910 [2].

There is no information in the literature on the condensation of 4,4'-diaminoazobenzene (1) and 4,4'-diaminostilbene (2) with β-acyloxybenzaldehydes (3–6 and 7–10).

Liquid crystalline compounds with two mesogenic moieties which are separated by a spacer ("twins"), containing azobenzene and stilbene units (11–14, 15–18 and 19, 20) are also unknown.

The synthesized compounds and polymers show the following principle structure:

By condensation of 4-hydroxybenzaldehyde with the acylchlorides CH$_3$-(CH$_2$)$_n$-COCl ($n = 4$, 6, 8, 10), the corresponding 4-acyloxybenzaldehydes 40–43 were prepared. By reacting of 40–43 with 1 the compounds 3–6 and with 2 the compounds 7–10 (type A) were obtained.

By condensation of p-hydroxybenzaldehyde with the alkanedicarboxylic acid dichlorides C$_{10}$C-(CH$_2$)$_n$-COCl ($n = 4$, 6, 8, 10) the corresponding alkanedicarboxylic acid bis(4-formylphenylesters) 36–39 were prepared. By reaction of 36–39 with 4-aminoazobenzene (31) and 4-aminostilbene (32) we got the compounds 11–14 (type B).

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The compounds 3–20 form yellow to orange coloured crystals and can be purified by recrystallization from glacial acetic acid or dimethylformamide. They are the model compounds for the following described polymers 21–28.

The polymers 21–28 were prepared by polycondensation in the solution of 1 and 2 with the alkanedicarboxylic bis(4-formylphenyl)esters.

The structure of all compounds and polymers was confirmed by elemental analyses, IR-spectroscopy and mass spectrometry.

Results

The model compounds 3–18 are liquid crystalline compounds. No mesophase was observed at 19 and 20 (Table I). 3–10 are enantiotropic smec-
Table I. Thermic behaviour of the model compounds 3–20 and the polymers 21–30; C = crystal phase, S = smectic phase, N = nematic phase, I = isotropic melt, So = solid phase (polymers), Meso = unknown mesophase.

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<thead>
<tr>
<th>No.</th>
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<td>4</td>
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<td>30</td>
<td>So/370 (dec.)/I</td>
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The compounds 11–18 are nematic. Monotropic phases were not observed.

In the Figures 1 to 4 the phase diagrams of the compounds 3–6, 7–10, 11–14 and 15–18 are shown. The mesophases were identified by polarizing microscopy under crossed Nichols. The phases have to be determined exactly by X-ray diffraction.

Fig. 2. Phase diagram of the 4,4'-bis(p-alkylcarbonyl-oxybenzylideneamino)azobenzenes 7–10. ○ melting point; + transition point; × clearing point.

Fig. 3. Phase diagram of the alkanediacid-bis-[4-N-(phenylazophenyl)iminoethyl]phenyl esters 11–14. ○ melting point; + transition point; × clearing point.

Fig. 1. Phase diagram of the 4,4'-bis(p-alkylcarbonyl-oxybenzylideneamino)azobenzenes 3–6. ○ melting point; + transition point; × clearing point.
Fig. 4. Phase diagram of the alkanediacid-bis[4-N-(4-styrylphenyl)iminomethyl]phenyl esters 15–18. ○ melting point; + transition point; × clearing point.

It was not possible to investigate the melting and transition temperatures of the polymers 21–30 with the heating rates of the model compounds (10 K/min), because of the decomposition of these polymers at these heating rates while DSC-measurements were carried out.

We investigated these polymers with the standard-DTA cell from Heraeus with heating rates of 100 K/min and received the following transition points (Table I). The measurements were performed up to 500 °C but in spite of the high heating rates the transition and clearing points could not been determined exactly.

From all compounds mass spectra were taken for studying the thermal degradation. Because most of the compounds and polymers decompose at higher temperatures, we were interested to study the decomposition of the molecules.

It is very typical for the decomposition to start at the ester bond. Within the groups of model compounds and polymers the mass spectra show the same scheme of fragmentation, differentiated only by the length of the alkyene moiety and the mole-peak.

An example of the degradation of the hexanediacid bis(4-N-(4-styrylphenyl)iminomethylphenyl)ester is given in Fig. 5. Table II and Table III explain the same fragmentation within one group of compounds.

Table II. Mass spectra of the poly(oxy-1,4-phenylene-methylidenenitrilo-1,4-phenyleneazo-1,4-phenylene-nitrilomethylidene-1,4-phenyleneoxy carbonyl-n*-methylenecarbonyls) 21–24. -n* = tetra (21), hexa (22), octa (23), deca (24).

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Fig. 5. Fragmentation scheme of 15, recorded at 260 °C.
Table III. Mass spectra of the poly(oxy-1,4-phenylene-
methylidenenitrilo-1,4-phenylenevinylene-1,4-phenylene-
nitrilomethylidene-1,4-phenyleneoxycarbonyl-n*-methy-

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Discussion

All prepared compounds have stiff and planar mesogenic groups with three or four aromatic ring systems. The colour is caused by the conjugation between the aromatic ringsystem and the azomethine, vinylene and azo links.

Decomposition occurs on all compounds near to or at the clearing point.

The temperature range of the mesophases is determined by the melting and clearing points of the known liquid crystalline compounds.

![Chemical structure](attachment:image.png)

trans-4,4'-bis (benzylideneamino) azobenzene (34)
K / 198 / N / 300 / I (dec.)

![Chemical structure](attachment:image.png)

trans-4,4'-bis (benzylideneamino) stilbene (35)
K / 267 / N / 322 / I (dec.)

These compounds also decompose in the nematic phase. The melting and transition temperatures of 3–18 decrease with increasing even numbered methylene units in the average of 6–7.5 °C per methylene unit.

The temperature range of the nematic phase is nearly constant within the groups (3–6, 7–10, 11–14 and 15–18). There is no influence by the spacer length but it does correspond to the nematic range of the compounds 34 and 35.

The compounds 11–18 with the stiff mesogenic groups at both ends, separated by a spacer (type B; “twins”) are thermally less stable than the compounds 3–10 with free rotating alkyl chains at both ends (type A).

“Pre-melting” has been observed for 15–18 during DSC-measurements, and identified as a solid-solid-transition by microscopic observation with polarized light. The type of transition will be determined by X-ray analysis.

Between 130 °C and 150 °C endothermic transitions have been seen. This can be explained by the rotation of long alkyl chains.

The compounds 7–10 have a nematic and one or more smectic phases. The smectic part grows with the increasing number of methylene units, in agreement with the results of other authors [6]. Only the polymers 27 and 28 show a mesophase between 320 °C and 333 °C (27) and between 320 °C and 380 °C (28).

Experimental Part

The elemental analyses were made in the Laboratory of Microanalysis at the Institute of Organic Chemistry of the FU Berlin. IR spectra were taken as KBr discs with a Perkin-Elmer 580B spectrometer. Mass spectra were taken by a Varian MAT-711 spectrometer. Because of the insolubility of the prepared compounds and polymers it was not possible to take 1H NMR spectras.

The melting and clearing points were determined with the DSC-system TA 500 S/2 from Heraeus (Hanau, BRD).

The textures were analyzed with crossed Nichols and photographed with the microscope “Universal” from C. Zeiss (Oberkochen, BRD). The declared yields are crude yields.

trans-4,4'-Diaminoazobenzene (1)

1 was obtained by mild reduction of a mixture of 4,4'-dinitroazobenzene and 4,4'-dinitrooxybenzene according to the instruction from N. Witt [7].
Violet-greenish needles from ethanol, m.p.: 250 °C (lit. [7]: 250–251 °C), yield: 84%.

\[ \text{C}_2\text{H}_2\text{N}_2 \text{O}_2 (212.3) \]
Calcd C 67.84 H 5.69 N 26.39,  
Found C 67.26 H 5.62 N 26.10.

IR (KBr), (cm\(^{-1}\)) = 3380 (m) \( \text{N-H}_2\text{val} \); 3070, 3050 (w) C–H arom; 1620 (s) C=\( \text{C-aro}_\text{m} \); 1595 (m) \( \text{-N-H}_2\text{stretch} \); 1505 (s) C=\( \text{C-Ar}_\text{val} \); 840 (s) Ar–H\( _p\)-disubst.

trans-4,4′-Diaminostilbene (2)
2 was obtained by a modified Wolff-Kishner reduction according to the method of Huang-Minlon [8].

Yellow needles from ethanol, m.p.: 227–228 °C (lit. [8]: 227–228 °C), yield: 40% after sublimation.

\[ \text{C}_{14}\text{H}_{14}\text{N}_2 (210.0) \]
Calcd C 80.00 H 6.67 N 13.33,  
Found C 79.79 H 6.63 N 13.58.

IR (KBr), (cm\(^{-1}\)) = 3390 (s), 3300 (s), 3210 (s) \( \text{N-H}_2\text{val} \); 3030 (w) C=\( \text{C-val} \); 1605 (s) \( \text{N-H}_2\text{stretch} \); 1515 (s) C=\( \text{C-Ar}_\text{val} \); 970 (s) CH=CH\( _\text{trans} \); 830 (s) \( \text{Ar-H}_p\)-disubst.

\( p \)-Aminostilbene (32)
32 was available by reduction of \( p \)-nitrostilbene according to the method of Pfeiffer et al. [9].

Long yellow needles from ethanol, m.p.: 151–152 °C (lit. [9]: 151–152 °C), yield: 55%.

\[ \text{C}_{14}\text{H}_{13}\text{N} (195.1) \]
Calcd C 86.15 H 6.66 N 13.18,  
Found C 86.12 H 6.74 N 7.08.

IR (KBr), (cm\(^{-1}\)) = 3390 (s), 3300 (s), 3205 (m) \( \text{NH}_2\text{val} \); 3030 (w) C=\( \text{C-val} \); 1605 (s) \( \text{NH}_2\text{stretch} \); 1515 (s) C=\( \text{C-Ar}_\text{val} \); 970 (s) CH=CH\( _\text{trans} \); 830 (s) Ar–H\( _p\)-disubst.; 730 (m) Ar–H\( _\text{monosubst} \).

General synthesis of the \( p \)-formylphenylesters 36–43
The \( p \)-formylphenylesters were prepared according to Einhorn [10] by alcoholysis of the corresponding carboxylic acid chlorides and dicarboxylic acid dichlorides in dry pyridine as the solvent and DMF as the catalyst. The acid chlorides have been prepared with PCl\textsubscript{3} and the corresponding carboxylic acids. The \( p \)-formylphenylesters 36–43 were recrystallized from ethanol and characterized by elemental analyses and IR spectroscopy.

**Bis(4-formylphenyl) hexanedioate (36)**
From 12.2 g (0.1 mol) \( p \)-hydroxybenzaldehyde and 9.1 g (0.05 mol) 1,4-butandicarboxylic dichloride; colourless fine crystals; m.p.: 90 °C; yield: 13.45 g (76%).

\[ \text{C}_{20}\text{H}_{18}\text{O}_6 (354.1) \]
Calcd C 67.80 H 5.08,  
Found C 68.17 H 5.07.

**Bis(4-formylphenyl) octanedioate (37)**
From 12.2 g (0.1 mol) \( p \)-hydroxybenzaldehyde and 10.5 g (0.05 mol) 1,4-octandicarboxylic dichloride; colourless fine crystals; m.p.: 90 °C; yield: 16 g (84%).

\[ \text{C}_{22}\text{H}_{22}\text{O}_6 (382.2) \]
Calcd C 69.10 H 6.34,  
Found C 69.42 H 6.71.

**Bis(4-formylphenyl) decanedioate (38)**
From 12.2 g (0.1 mol) \( p \)-hydroxybenzaldehyde and 11.9 g (0.05 mol) 1,4-decanedicarboxylic dichloride; colourless fine crystals; m.p.: 75 °C; yield: 13.7 g (67%).

\[ \text{C}_{24}\text{H}_{26}\text{O}_6 (410.2) \]
Calcd C 70.24 H 6.34,  
Found C 70.43 H 6.40.

**Bis(4-formylphenyl) dodecanedioate (39)**
From 12.2 g (0.1 mol) \( p \)-hydroxybenzaldehyde and 13.3 g (0.05 mol) 1,4-dodecanedicarboxylic dichloride; colourless fine crystals; m.p.: 87 °C; yield: 17.5 g (80%).

\[ \text{C}_{26}\text{H}_{30}\text{O}_6 (438.2) \]
Calcd C 71.23 H 6.85,  
Found C 70.92 H 6.91.

**4-Formylphenylhexanoate (40)**
From 12.2 g (0.1 mol) \( p \)-hydroxybenzaldehyde and 13.5 g (0.1 mol) hexanoyl chloride; m.p.: 0–20 °C; yield: 20.9 g (95%).

\[ \text{C}_{13}\text{H}_{16}\text{O}_3 (220.1) \]
Calcd C 70.91 H 7.27,  
Found C 70.78 H 7.35.

**4-Formylphenyloctanoate (41)**
From 12.2 g (0.1 mol) \( p \)-hydroxybenzaldehyde and 16.3 g (0.1 mol) octanoyl chloride; m.p.: 0–20 °C; yield: 22.3 g (90%).

\[ \text{C}_{15}\text{H}_{20}\text{O}_3 (248.2) \]
Calcd C 72.58 H 8.06,  
Found C 72.68 H 8.23.
4-Formylphenyldecanoate (42)
From 12.2 g (0.1 mol) \( p \)-hydroxybenzaldehyde and 19.0 g (0.1 mol) decanoyl chloride; m.p.: 0–20 °C; yield: 26 g (94%).
\[ \text{C}_{17}H_{14}O_3 (276.2) \]
Calcd C 73.91 H 8.70, Found C 73.63 H 8.78.

4-Formylphenyldodecanoate (43)
From 12.2 g (0.1 mol) \( p \)-hydroxybenzaldehyde and 21.9 g (0.1 mol) dodecanoyl chloride; m.p.: 0–20 °C; yield: 29.2 g (96%).
\[ \text{C}_{19}H_{28}O_3 (304.2) \]
Calcd C 75.00 H 9.21, Found C 75.33 H 9.35.

General synthesis of the 4,4'-bis(4-alkylcarbonyloxybenzylideneamino)azobenzenes 3–6, the 4,4'-bis(4-alkylcarbonyloxybenzylideneamino)-stilbenes 7–10, the alkanediacid-bis{4-N-(4-phenylazophenyl)iminomethylphenyl}esters 11–14, the alkanediacid-bis{4-N-(4-styrylphenyl)iminomethylphenyl}esters 15–18, 1,6-di[5-{N-(4-phenylazophenyl)iminomethyl}-2-thienyl]hexane 19, 1,6-di[5-{N-(4-styrylphenyl)iminomethyl}-2-thienyl]hexane 20 and the polymers 21–28.

For preparing the low molecular weight and polymeric Schiff bases, the amino and carbonyl compounds were refluxed for 4 h in a dry solvent at 109 °C (toluene for the low molecular Schiff bases) and 153 °C (dimethyl formamide for the polymers). The reaction product was allowed to cool down to room temperature and the precipitate was filtered by means of vacuum and recrystallized from glacial acetic acid or dimethyl formamide (3–20). The polymers were extracted with boiling ethanol and then DMF.

4,4'-Bis(4-pentylcarbonyloxybenzylideneamino)-azobenzene (3)
From 0.265 g (1.25 mmol) 1 and 0.550 g (2.5 mmol) 40 in toluene for 4 h; m.p.: 267 °C, orange needles from DMF; yield: 0.40 g (53%).
\[ \text{C}_{38}H_{40}N_4O_4 (616.3) \]
Calcd C 73.98 H 6.54 N 9.09, Found C 73.66 H 6.66 N 9.04.

IR (KBr), (cm\(^{-1}\)) = 3070 (w) \( \text{C-H} \) val; 3040 (w) \( \text{Ar-H} \); 2960 (s), 2930 (s), 2880 (s) \( \text{C-H} \) val; 1755 (s) \( \text{C=O} \); 1625 (m) \( \text{C=O} \); 1600 (m), 1575 (s), 1505 (s) \( \text{Ar-H} \); 1205, 1160, 1135, 1110 (s) \( \text{C=O} \); 860 (s) \( \text{Ar-H} \); 730 (w) \( \text{CH}_2 \) rocking; 570 (s) \( \text{Ar-H} \).

These absorptions are also typical for 4–6.

4,4'-Bis(4-heptylcarbonyloxybenzylideneamino)-azobenzene (4)
From 0.265 g (1.25 mmol) 1 and 0.620 g (2.5 mmol) 41 in toluene for 4 h; m.p.: 330 °C, orange needles from DMF; yield: 0.51 g (60.7%).
\[ \text{C}_{45}H_{58}N_4O_4 (672.4) \]
Calcd C 74.95 H 7.19 N 8.33, Found C 74.87 H 7.27 N 8.41.

4,4'-Bis(4-nonylcarbonyloxybenzylideneamino)-azobenzene (5)
From 0.265 g (1.25 mmol) 1 and 0.690 g (2.5 mmol) 42 in toluene for 4 h; m.p.: 303 °C, orange needles from DMF; yield: 0.71 g (65%).
\[ \text{C}_{50}H_{66}N_4O_4 (728.9) \]
Calcd C 75.77 H 7.75 N 7.69, Found C 75.64 H 7.99 N 7.70.

4,4'-Bis(4-undecylcarbonyloxybenzylideneamino)-azobenzene (6)
From 0.265 g (1.25 mmol) 1 and 0.760 g (2.5 mmol) 43 in toluene for 4 h; m.p.: 299 °C, orange needles from DMF; yield: 0.75 g (64%).
\[ \text{C}_{55}H_{74}N_4O_4 (784.5) \]
Calcd C 76.47 H 8.22 N 7.14, Found C 76.71 H 8.54 N 6.91.

4,4'-Bis(4-pentylcarbonyloxybenzylideneamino)-stilbene (7)
From 0.315 g (1.25 mmol) 2 and 0.556 g (2.5 mmol) 40 in toluene for 4 h; m.p.: 335 °C, yellow needles from DMF; yield: 0.60 g (65%).
\[ \text{C}_{40}H_{32}N_4O_4 (614.3) \]
Calcd C 78.13 H 6.89 N 4.56, Found C 79.04 H 6.93 N 4.51.

IR (KBr), (cm\(^{-1}\)) = 3030 (w) \( \text{Ar-H} \); 2960, 2940, 2880 (m/s) \( \text{C-H} \) val; 1750 (s) \( \text{C=O} \); 1625 (m) \( \text{C=O} \); 1600, 1580 (m), 1510 (s) \( \text{Ar-H} \); 1380 (m) \( \text{C=CH}_3 \) symm def; 1250, 1210, 1160, 1110 (s) \( \text{C=O} \); 970 (m) \( \text{C=O} \); 850 (s) \( \text{Ar-H} \); 730 (w) \( \text{CH}_2 \) rocking; 560 (s) \( \text{Ar-H} \).

These absorptions are also typical for 8–10.

4,4'-Bis(4-heptylcarbonyloxybenzylideneamino)-stilbene (8)
From 0.315 g (1.25 mmol) 2 and 0.620 g (2.5 mmol) 41 in toluene for 4 h; m.p.: 324 °C, yellow needles from DMF; yield: 0.72 g (72%).
\[ \text{C}_{46}H_{58}N_4O_4 (670.4) \]
Calcd C 78.75 H 7.52 N 4.18, Found C 78.93 H 7.43 N 4.12.
4,4'-Bis(4-nonylcarbonyloxybenzylideneamino)-stilbene (9)

From 0.315 g (1.25 mmol) 2 and 0.690 g (2.5 mmol) 42 in toluene for 4 h; m.p.: 332 °C, yellow needles from DMF; yield: 0.78 g (72%).

C_{48}H_{55}N_{2}O_{4} (726.5)
Calcd C 79.29 H 8.04 N 3.86,
Found C 79.62 H 7.98 N 3.86.

4,4'-Bis(4-undecylcarbonyloxybenzylideneamino)-stilbene (10)

From 0.315 g (1.25 mmol) 2 and 0.760 g (2.5 mmol) 43 in toluene for 4 h; m.p.: 322 °C, yellow needles from DMF; yield: 0.96 g (82%).

C_{52}H_{66}N_{2}O_{4} (782.5)
Calcd C 79.74 H 8.50 N 3.58,
Found C 79.75 H 8.46 N 3.52.

Hexanediacid-bis{4-N-(4-phenylazophenyl)imino-methylphenyl}ester (11)

From 0.493 g (2.5 mmol) 31 and 0.442 g (1.25 mmol) 36 in toluene for 4 h; m.p.: 323 °C, orange needles from DMF; yield: 0.86 g (97%).

C_{44}H_{36}N_{6}O_{4} (712.3)
Calcd C 74.12 H 5.09 N 11.80,
Found C 73.85 H 5.12 N 11.70.

IR (KBr), (cm⁻¹) = 3070 (w) C-H val; 3040 (w) Ar-H val; 2950, 2880 (w) C-H val; 1755 (s) C=O ester; 1625 (m) C=N conj; 1600, 1575, 1505 (s) Ar-H; 1250, 1200, 1160, 1130 (s) C=O val; 967 (m) C=CHtrans, def.; 865 (m) Ar-H_{1-4} disubst.; 690 (s) Ar-H_{monosubst.}.

These absorptions are also typical for 12-14.

Octanediacid-bis{4-N-(4-phenylazophenyl)imino-methylphenyl}ester (12)

From 0.493 g (2.5 mmol) 31 and 0.478 g (1.25 mmol) 37 in toluene for 4 h; m.p.: 330 °C, yellow needles from DMF; yield: 0.65 g (71%).

C_{50}H_{46}N_{6}O_{4} (736.4)
Calcd C 81.36 H 5.98 N 3.80,
Found C 81.20 H 6.15 N 3.80.

Decanediacid-bis{4-N-(4-phenylazophenyl)imino-methylphenyl}ester (13)

From 0.493 g (2.5 mmol) 31 and 0.512 g (1.25 mmol) 38 in toluene for 4 h; m.p.: 300 °C, yellow needles from DMF; yield: 0.67 g (70%).

C_{52}H_{48}N_{6}O_{4} (764.4)
Calcd C 81.52 H 6.15 N 3.66,
Found C 81.37 H 6.36 N 3.62.

Dodecanediacid-bis{4-N-(4-phenylazophenyl)imino-methylphenyl}ester (14)

From 0.493 g (2.5 mmol) 31 and 0.548 g (1.25 mmol) 39 in toluene for 4 h; m.p.: 264 °C, yellow needles from DMF; yield: 0.72 g (73%).

C_{54}H_{52}N_{6}O_{4} (792.4)
Calcd C 81.77 H 6.62 N 3.53,
Found C 81.53 H 6.60 N 3.57.
1,6-Bis[5-(N-(4-phenylazophenyl)iminomethyl)-2-thienyl]hexane (19)

From 0.493 g (2.5 mmol) 31 and 0.396 g (1.25 mmol) 33 in toluene for 4 h; m. p.: 187 °C, orange needles from DMF; yield: 0.60 g (72%).

C_{40}H_{36}N_{6}S_{2} (664.5)
Calcd C 72.23 H 5.46 N 12.65,
Found C 71.89 H 5.87 N 12.18.

IR (KBr), (cm^{-1}) = 3040 (w) Ar-H val; 2935, 2860 (m) C-H val; 1615 (m) C=NOH; 1585 (s) Ar-H; 1470 (s) CH_{2}val; 850 (s) Ar-H, 4disubst; 770 (s) Ar-H monosubst; 730 (w) CH_{2} rocking; 690 (s) ArH monosubst.

1,6-Bis[5-(N-(4-styrylphenyl)iminomethyl)-2-thienyl]hexane (20)

From 0.487 g (2.5 mmol) 32 and 0.396 g (1.25 mmol) 33 in toluene for 4 h; m. p.: 235 °C, yellow needles from DMF; yield: 0.70 g (85%).

C_{44}H_{40}N_{6}S_{2} (660.5)
Calcd C 79.94 H 6.10 N 4.24,
Found C 79.84 H 6.10 N 4.24.

IR (KBr), (cm^{-1}) = 3060 (w) C-H val; 3030 (w) Ar-H val; 2940, 2880 (w) CHval; 1615 (s) C=CN conj; 1575 (s), 1505 (m) Ar-H; 970 (s) C=C trans-def; 870 (m) Ar-H, 4disubst; 755 (m/s) Ar-H monosubst; 690 (s) Ar-H monosubst.

Poly(oxy-1,4-phenylenemethylenenitrilo-1,4-phenyleneaizo-1,4-phenylenenitrilomethylidene-1,4-phenylenoeycarbonyltetramethylenecarbonyl) (21)

From 0.530 g (2.5 mmol) 1 and 0.884 g (2.5 mmol) 36 in dimethylformamide for 4 h; m. p.: >370 °C (dec.); yellowish-brown, “brick-dust” like; yield: 1.12 g (84.5%).

(C_{32}H_{26}N_{2}O_{4})_{n} (530.2)_{n}
Calcd C 72.42 H 4.94 N 10.56,
Found C 71.50 H 5.13 N 10.36.

IR (KBr), (cm^{-1}) = 3380 (w) N-H val; 3030 (w) Ar-H val; 2940, 2880 (w) C-H val; 1755 (s) C=O ester; 1700 (m) C=O aldehyde; 1625 (s) C=N conj; 1600 (m); 1580 (s) Ar-H; 1250 (m), 1200, 1160, 1120 (s) C=O val; 850 (s) Ar-H monosubst.

These absorptions are also typical for 22-24.

Poly(oxy-1,4-phenylenemethylenenitrilo-1,4-phenyleneaizo-1,4-phenylenenitrilomethylidene-1,4-phenylenoeycarbonyloctamethylenecarbonyl) (22)

From 0.530 g (2.5 mmol) 1 and 1.025 g (2.5 mmol) 37 in dimethylformamide for 4 h; m. p.: 310 °C, yellowish-brown, “brick-dust” like; yield: 1.16 g (83%).

(C_{34}H_{30}N_{4}O_{4})_{n} (558.3)_{n}
Calcd C 73.08 H 5.42 N 10.03,
Found C 71.11 H 5.64 N 11.48.

Poly(oxy-1,4-phenylenemethylenenitrilo-1,4-phenyleneaizo-1,4-phenylenenitrilomethylidene-1,4-phenylenoeycarbonyloctamethylenecarbonyl) (23)

From 0.530 g (2.5 mmol) 1 and 1.025 g (2.5 mmol) 38 in dimethylformamide for 4 h; m. p.: 320 °C, yellowish-brown, “brick-dust” like; yield: 1.17 g (80%).

(C_{36}H_{34}N_{2}O_{4})_{n} (586.3)
Calcd C 73.68 H 5.84 N 9.55,
Found C 71.86 H 6.04 N 9.61.

Poly(oxy-1,4-phenylenemethylenenitrilo-1,4-phenyleneaizo-1,4-phenylenenitrilomethylidene-1,4-phenylenoeycarbonyldecamethylenecarbonyl) (24)

From 0.530 g (2.5 mmol) 1 and 1.095 g (2.5 mmol) 39 in dimethylformamide for 4 h; m. p.: 240 °C, yellowish-brown, “brick-dust” like; yield: 1.32 g (86%).

(C_{38}H_{38}N_{2}O_{4})_{n} (614.3)
Calcd C 74.23 H 6.23 N 9.12,
Found C 72.42 H 6.52 N 9.47.

Poly(oxy-1,4-phenylenemethylenenitrilo-1,4-phenyleneaizo-1,4-phenylenenitrilomethylidene-1,4-phenylenoeycarbonyltetramethylenecarbonyl) (25)

From 0.630 g (2.5 mmol) 2 and 0.884 g (2.5 mmol) 36 in dimethylformamide for 4 h; m. p.: >370 °C (dec.), dark yellow, “brick-dust” like; yield: 1.14 g (86%).

(C_{34}H_{26}N_{2}O_{4})_{n} (528.2)
Calcd C 77.24 H 5.34 N 5.30,
Found C 75.96 H 5.38 N 5.30.

IR (KBr), (cm^{-1}) = 3380 (w) N-H val; 3030 (w) Ar-H val; 2940, 2880 (w) C-H val; 1755 (s) C=O ester; 1700 (m) C=O aldehyde; 1625 (s) C=N conj; 1600 (m); 1580 (s) Ar-H; 1250 (m), 1200, 1160, 1120 (s) C=O val; 850 (s) Ar-H monosubst.
1700 (m) C=O aldehyde; 1625 (s) C=N conj.; 1600 (m), 1580 (s) Ar-H; 1250 (m), 1200, 1160, 1120 (s) C=C-trans, 850 (s) Ar-H, 4 disubst. These absorptions are also typical for the polymers 26-28.

Poly(oxy-1,4-phenylenemethylidenenitrilo-1,4-phenylenevinylene-1,4-phenylenenitrilomethyliden-1,4-phenyleneoxycarbonylhexamethylene carbonyl) (26)

From 0.630 g (2.5 mmol) 2 and 0.955 g (2.5 mmol) 37 in dimethylformamide for 4 h; m.p.: >370 °C (dec.), dark yellow, “brick-dust” like; yield: 1.17 g (84%).

(C_{36}H_{32}N_{2}O_{4})_{n} (556.3),
Calcd C 77.66 H 5.80 N 5.03,
Found C 76.79 H 5.84 N 5.49.

Poly(oxy-1,4-phenylenemethylidenenitrilo-1,4-phenylenevinylene-1,4-phenylenenitrilomethyliden-1,4-phenyleneoxycarbonyloctamethylene carbonyl) (27)

From 0.630 g (2.5 mmol) 2 and 1.025 g (2.5 mmol) 38 in dimethylformamide for 4 h; m.p.: 333 °C (dec.), dark yellow, “brick-dust” like; yield: 1.07 g (73%).

(C_{38}H_{36}N_{2}O_{4})_{n} (584.3),
Calcd C 78.04 H 6.21 N 4.79,
Found C 76.22 H 6.20 N 4.91.

Poly(oxy-1,4-phenylenemethylidenenitrilo-1,4-phenylenevinylene-1,4-phenylenenitrilomethyliden-1,4-phenyleneoxycarbonyldecamethylene carbonyl) (28)

From 0.630 g (2.5 mmol) 2 and 1.095 g (2.5 mmol) 39 in dimethylformamide for 4 h; m.p.: 380 °C (dec.), dark yellow, “brick-dust” like; yield: 1.38 g (90%).

(C_{40}H_{40}N_{2}O_{4})_{n} (612.3),
Calcd C 78.39 H 5.48 N 4.57,
Found C 77.12 H 6.64 N 4.85.

Poly(nitrilo-1,4-phenyleneazo-1,4-phenylenenitrilomethyliden-2,5-thiophenediyloctamethylene-carbonyl) (29)

From 0.630 g (2.5 mmol) 1 and 0.792 g (2.5 mmol) 33 in dimethylformamide for 4 h; m.p.: >300 °C (dec.), brownish, “brick-dust” like; yield: 1.14 g (95%).

(C_{30}H_{28}N_{2}S_{2})_{n} (480.4),
Calcd C 74.94 H 5.86 N 5.83,
Found C 72.61 H 6.06 N 6.15.

IR (KBr), (cm⁻¹) = 3380 (w) N-H val; 3030 (w) Ar-H val; 2950, 2880 (w) C-H val; 1665 (m) C=O aldehyde; 1615 (s) C=N conj; 1590 (s) Ar-H; 850 (s) Ar-H; 810 (m/s) thiophene, 2,5-disubst.

References:
[10] A. Einhorn, Liebigs Annalen 301, 95 (1898).