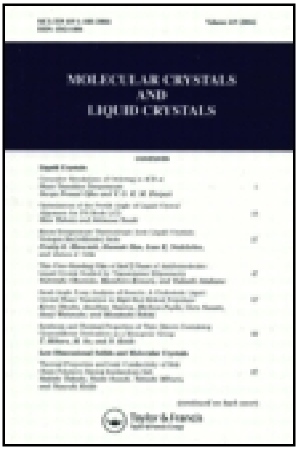

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Tris(Dialkylamino)-s-Triazines, Characterization and Thermal Properties

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Tris(Dialkylamino)-s-Triazines, Characterization and Thermal Properties

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Several Tris(dialkylamino)-s-triazines were prepared by reaction of cyanuric chloride with the appropriate secondary amines. Some of their properties are reported.

Keywords: tris(dialkylamino)-s-triazines, core-compounds, discophases, DSC, polarizing microscopy, whiskers

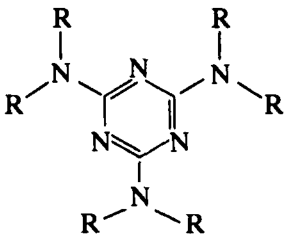
1. INTRODUCTION

Molecules with a central "core" and several moderately long side chains may exhibit interesting properties, e.g. alkali metal complexing behaviour of "octopus"-molecules[1] or formation of discotic mesophases. In disc-like mesogens at least three[2] and up to nine[3] aliphatic chains are linked to the central part by ether-, ester-, benzoate-, sulfon-,[4] sulfur-[5] or selengroups.[6] The cores are known to consist of rigid, flat rings (aromatic, heteroaromatic or metal complex),[7] aromatic rings with flexible segments (superdiscs)[3] or saturated alicyclics.[8] It was proposed[9] that the trisubstituted s-triazine-ring is favourable to give discophases.

Therefore we synthesized several 2,4,6-tris(dialkylamino)-s-triazines and characterized their thermal behaviour.

2. SYNTHESIS

In analogy to a previously described method[10] we prepared beside the known products 1 and 2 the new ones 3 and 4 by reacting cyanuric chloride with the appropriate dialkylamines in toluene at 110°C.



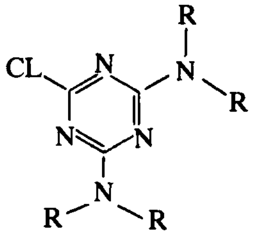
$R = -CH_2-CH-(CH_3)_2$ 1

$-CH_2)_7-CH_3$ 2

$-(CH_2)_9-CH_3$ 3

$-(CH_2)_{11}-CH_3$ 4

2,4-Bis(didodecylamino)-6-chlor-s-triazine 7 in contrast to 5 and 6 could easily be isolated by fractional precipitation from the appropriate reaction mixture.



$R = -(CH_2)_7-CH_3$ 5

$-(CH_2)_9-CH_3$ 6

$-(CH_2)_{11}-CH_3$ 7

The purity of the triazine derivatives was checked by means of gel permeation chromatography (GPC). In Figure 1 a, b the chromatogram of a mixture of 4 and 7 and that of pure compound 4 is shown as an example. Figure 2 illustrates the linear dependence between the logarithm of the molar mass lg M and elution volume V_e of compounds 2, 3, 4 and 5, 6, 7 respectively, typical for members of homologous series. The products were characterized by IR, NMR, mass spectrometry and elemental analysis.

3. PROPERTIES

Investigations of the products by means of DSC and the polarizing microscope gave no evidence for the existence of mesophases. The melting points are given in Table I.

1, though carrying only short paraffinic chains, was regarded to be an interesting compound, since the CPK-model shows the ability of

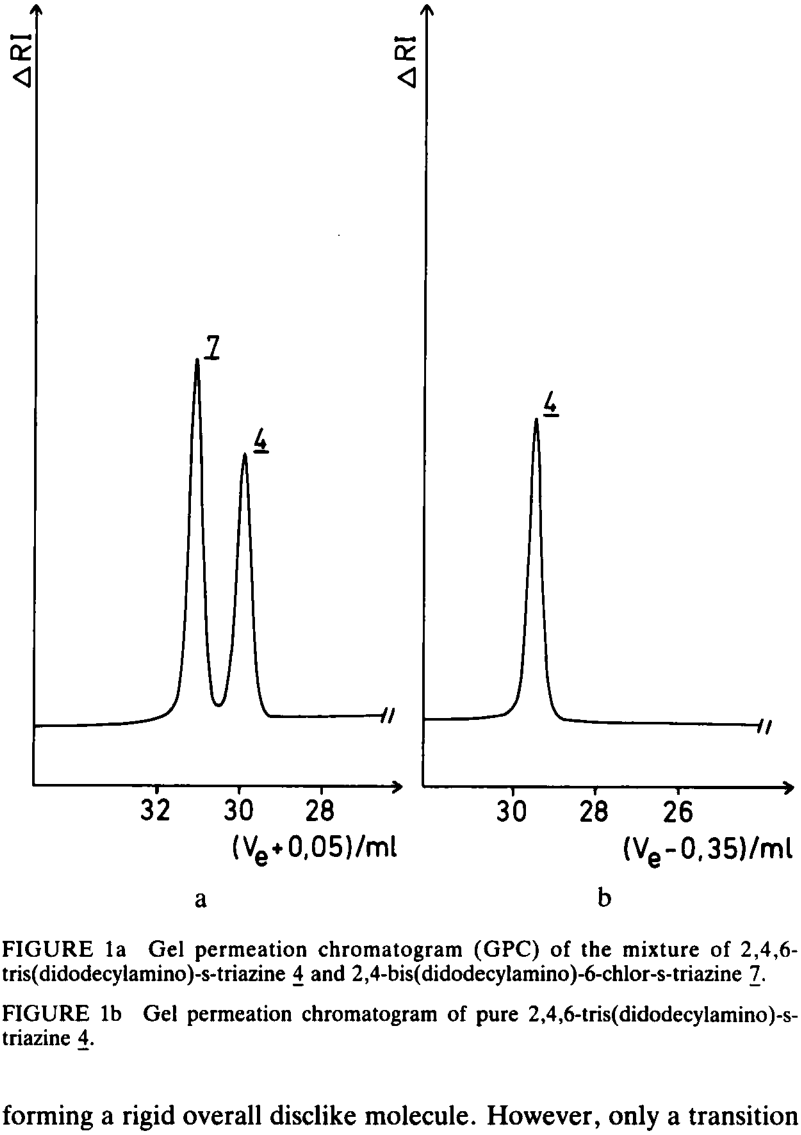


FIGURE 1a Gel permeation chromatogram (GPC) of the mixture of 2,4,6-tris(didodecylamino)-s-triazine 4 and 2,4-bis(didodecylamino)-6-chlor-s-triazine 7.

FIGURE 1b Gel permeation chromatogram of pure 2,4,6-tris(didodecylamino)-s-triazine 4.

forming a rigid overall disclike molecule. However, only a transition from a spherolithic (K_1) to a platelike (K_2) crystal modification could be observed at about 75°C when heating the previously molten and slowly cooled (1°C/min) product between glass slides under the polarizing microscope (1°C/min). Because of the slow transition rate from K_1 to K_2 the melting point T_{m1} of K_1 could be determined to be 81,7°C. During the melting process of K_1 the already formed crystals of K_2 show an unhindered growth from the melt of K_1 till

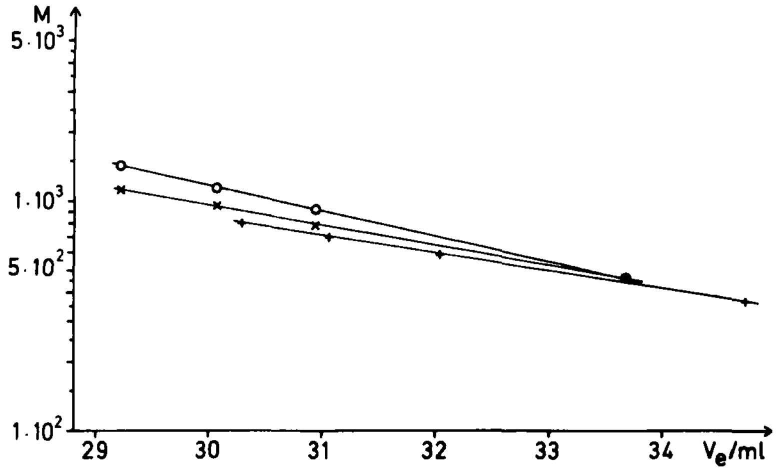


FIGURE 2 lgM - V_e - relationships of 2,4,6-tris(dialkylamino)-s-triazines (x) and 2,4-bis(dialkylamino)-6-chlor-s-triazines (+), compared with standard polystyrenes (o).

the melting point T_{m2} of K_2 at 99°C is reached. From DSC measurements of 1, treated in the same manner, neither the crystal transition nor T_{m1} were detected.

In the contrast to 1 crystals of 2, 3, and 4 exist in the form of very thin needles.

After melting at 38.9°C, 2 shows up on cooling a broad range of supercooling, and a very small crystallization rate i.e. it takes several hours to crystallize at 20°C. Shearing the melt between the glass slides at about 27°C induces rather quick growth of very thin long needles as observed under the polarizing microscope. Maintaining the temperature at the early growth stage, the needles begin to form helical

TABLE I

Melting points T_{m1}, T_m and recrystallization temperature T_{rc} of 2,4,6-tris(dialkylamino)-s-triazines. Temperatures are given in °C, melting enthalpies (ΔH) in KJ mol^{-1}

Compound	T_{m1}	T_{rc}	T_m	ΔH
1	81.7[a]		99.4[b]	35.81
2			39.5[c]	74.25
3			41.2	87.68
4	39.7	40.8	47.1	119.19
7			34.25	90.55

[a] taken from measurements under the polarizing microscope
[b] 91°C[10], [c] 32°C[10].

windings or even large rings of several turnings parallel to the plane of the glass slide.

3 shows a similar phenomenon: after melting at 40,3°C, quenching to 35°C and further cooling to 33°C (0.5°C/min) bent, flexible needles, wound-up needles forming helices and large rings show up, the helices and rings being even more pronounced as for 2 (Figure 3 a, b, c).

When 3 is quenched to 35°C, further cooled down to 33°C and than annealed at 39°C for several hours without cover glass, besides helices and rings, needles wind together to form hollow conical or cylindrical structures (Figure 4a,b). When looking at the hollow cones and cylinders in the direction of their longitudinal axis (Figure 3 c) or when the longitudinal growth of the cylinders is hindered by a cover glass (Figure 3 a) obviously only rings are observed as described above.

After melting at 47°C and quenching 4 shows shorter needles than 2 and 3, a number of them exhibiting a more helicoidal than a helical appearance. The rings are smaller and less numerous.

The crystallization temperature T_c observed during DSC cooling measurements shows a clear dependence on the temperature T_s, the highest temperature up to which the melt was heated.

T_c is the lower the higher T_s was. Further, when the melt was heated up to 57°C and higher, upon cooling a second and a third peak or shoulder appear, the respective temperatures T_c' and T_c'' being the lower the higher T_s was. In Table II the various temperatures are listed, in Figure 5 several cooling runs are shown as examples, in Figure 6 the dependence of T_c, T_c' and T_c'' on T_s is given. When 4 after a cooling run with a single crystallization peak is heated, a single melting peak is obtained (Figure 7). However, when 4 is heated after a cooling run with two or three crystallization peaks a small endotherm at $T_{m1} = 39.7°C$ and an exothermic recrystallization peak at $T_{rc} = 40{,}8°C$ appear (Figure 8). The small endotherm grows up, the exotherm disappears with increasing heating rate (Figure 9). Furthermore a shoulder in the melting peak above T_m can be observed.

4. DISCUSSION

The described needle shaped crystals are to be designated as whiskers.[11,12,13] They are 1 to 5 μm in diameter and up to one centimeter long. They grow in a supercooled melt with high rate along the whisker axis. They are very flexible. A helical or helicoidal growth is observed.

Whilst whisker growth has been observed mostly with inorganic compounds also a few examples of organic compounds have become known to form whiskers. Nabarro and Jackson[13] reported in 1958

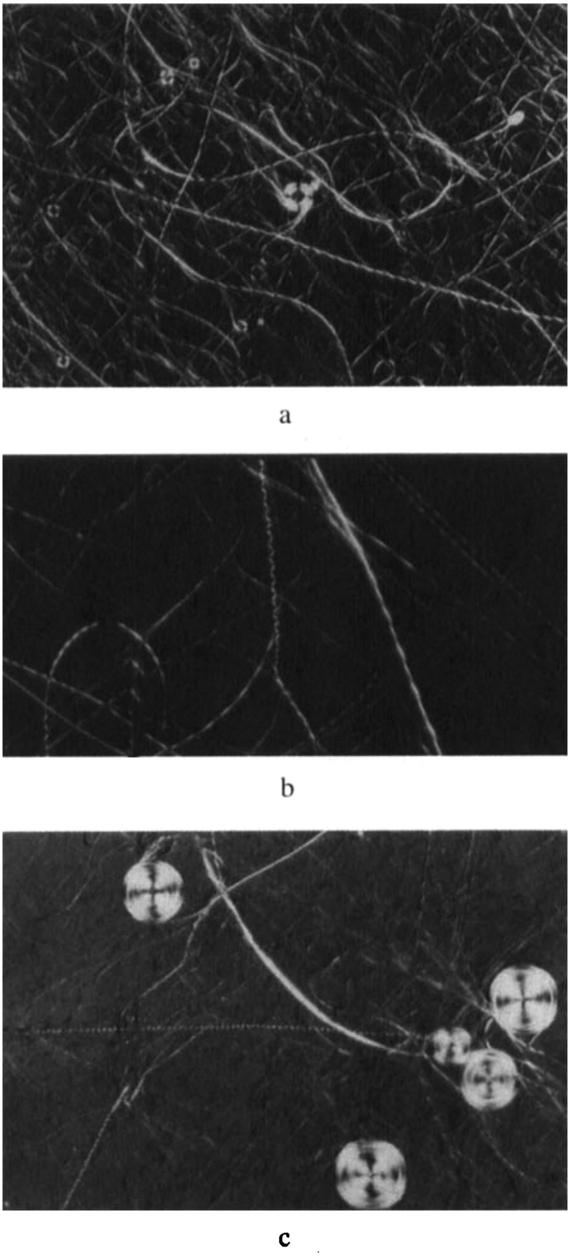


FIGURE 3 Bent, helical whiskers and rings of crystallized 2,4,6-tris(didecylamino)-s-triazine $\underline{3}$; a) 33°C, crossed polarizers, 96 fold magnif.; b) 38,4°C, crossed polarizers, 240 fold magnif.; c) 38,4°C, crossed polarizers, 96 fold magnif.; without cover glass.

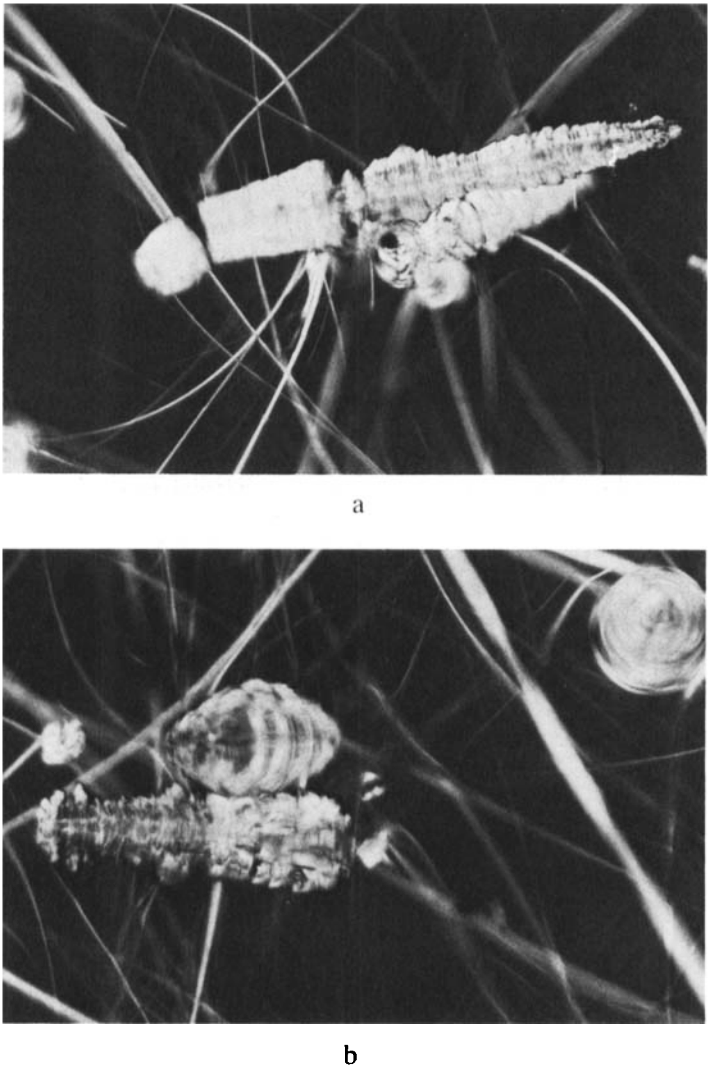


FIGURE 4 Hollow conical and cylindrical structures of crystallized 2,4,6-tris(didecylamino)-s-triazine 3; a) 39°C, crossed polarizers, 96 fold magnif. without cover glass; b) 39°C, crossed polarizers, 138 fold magnif.; without cover glass.

bending of whiskers of hexachlorobenzene as caused by a "characteristic defect of a crystal composed of piles of disc-shaped molecules," i.e. "the absence of an isolated molecule (slipped disc)" in the pile and the "accumulation" of this defect "on one side of the whisker." So we can assume that if not the liquid phase, then at least

TABLE II

Crystallization temperature T_c, T'_c and T''_c of 2,4,6-tris-(didodecylamino)-s-triazine 4 as a function of T_s, the temperature the melt was heated beyond the melting temperature. Temperatures are given in °C

T_s	T_c	T'_c	T''_c
51	33.1		
53	31.5		
55	31.0		
57	30.4	29.5	
58	30.2*	29.5*	27.8
60	29.8*	28.8	27.3
65	29.0*	27.7	26.5
70	28.5	27.5*	26.2
100	28.1	27.2	

*shoulder

the crystalline phase of the synthesized s-triazines might have a columnar structure. These whiskers therefore may represent a solid equivalent to the discotic liquid crystal fibres of hexa-alkoxytriphenylenes, obtained in nearly single crystal quality, having dimensions quite similar to those of whiskers.[14]

The dependence of the crystallization temperature T_c of 4 on T_s is interpreted as an athermic nucleation process, i.e. all crystallized

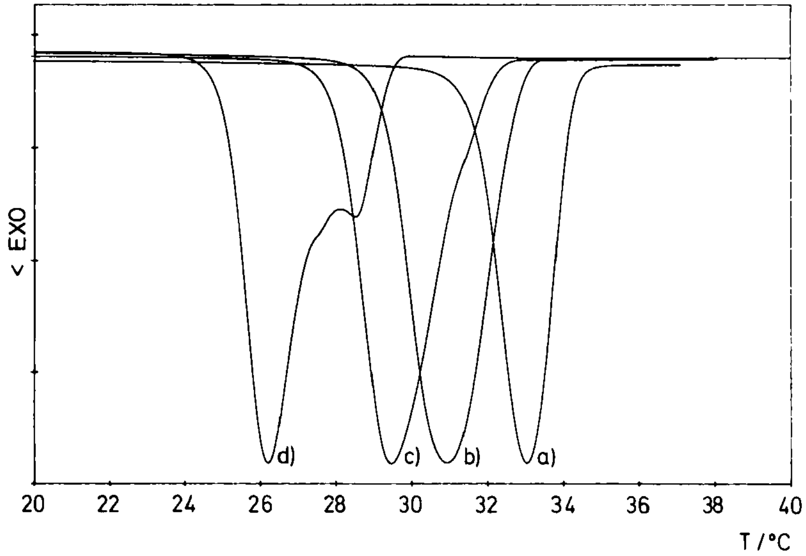


FIGURE 5 DSC thermograms of 4, cooling rate 10°C/min, for different T_s-values: 51°C (a), 55°C (b), 57°C (c), 70°C (d).

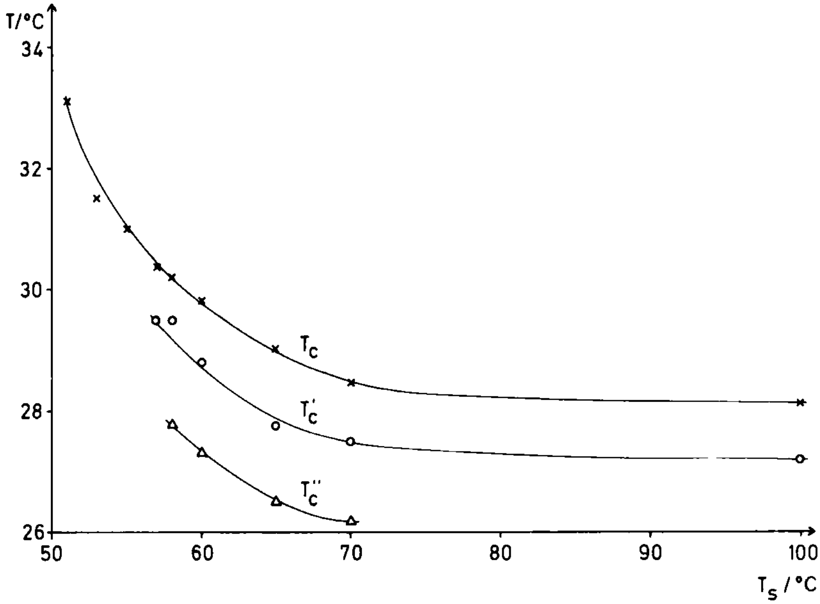


FIGURE 6 Relationship between crystallization temperature T_c (x), the supplementary temperatures T_c' (o) and T_c'' (△) and the temperature T_s.

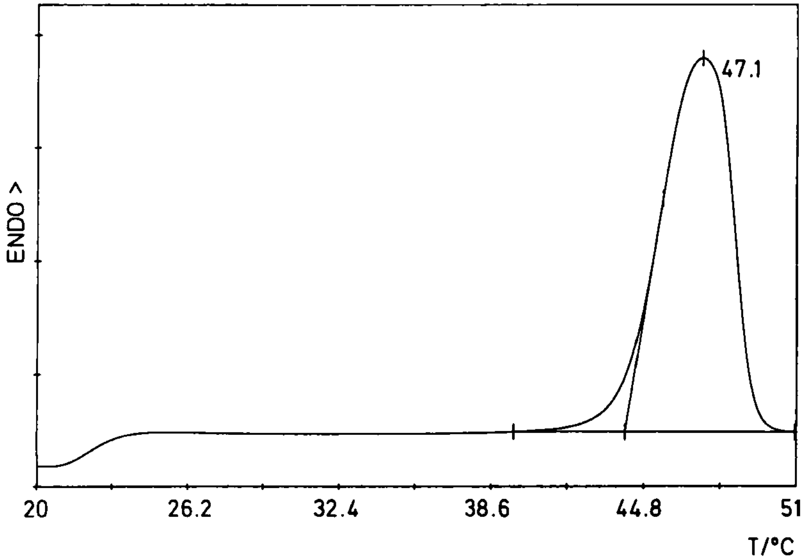


FIGURE 7 DSC thermogram of 4. Heating curve (10°C/min), taken after a cooling run, during which the sample showed one crystallization peak.

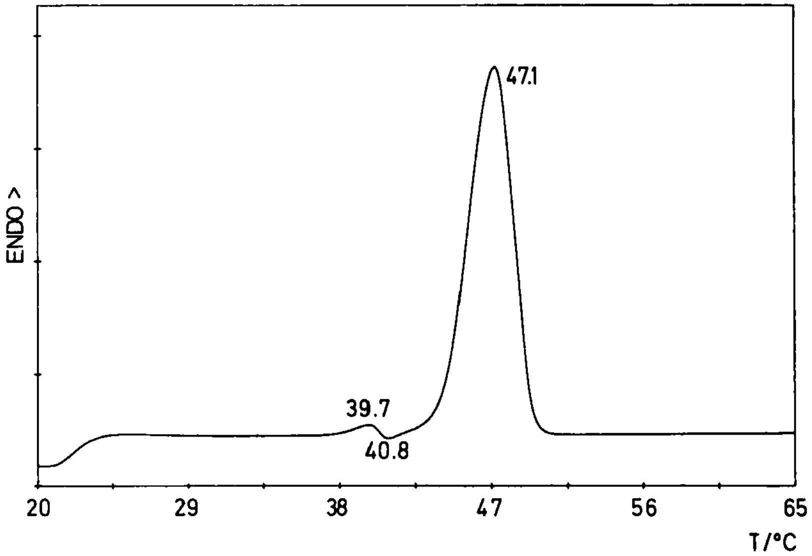


FIGURE 8 DSC thermogram of 4. Heating curve (10°C/min) taken after a cooling run, during which the sample showed three crystallization peaks resp. shoulders.

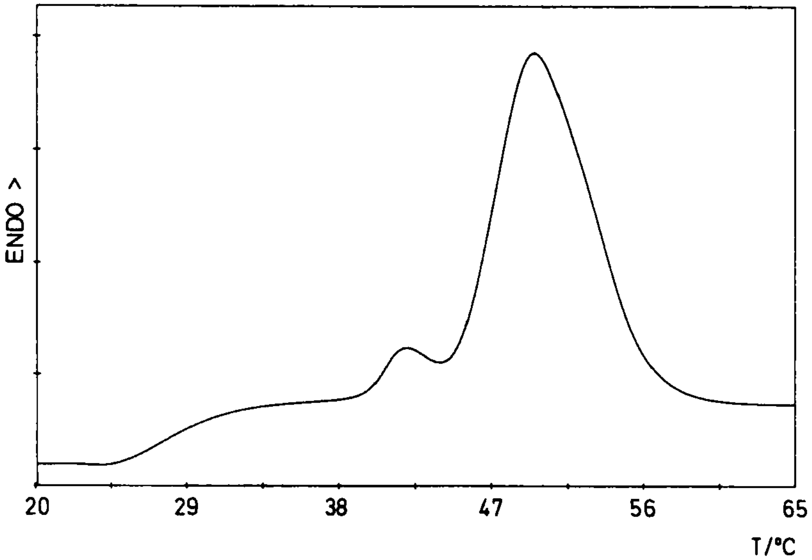


FIGURE 9 DSC thermogram of 4. Heating curve (50°C/min), taken after a cooling run, during which sample showed three crystallization peaks resp. shoulders.

material or nuclei having survived beyond the melting temperature, will be destroyed eventually when the melt is superheated. Examples of such a phenomenon are known in the fields of metals and macromolecules.[15] Secondly the higher T_s the more pronounced is the appearance of crystallization peaks at T_c' and T_c'' each of them showing a similar dependence on T_s as on T_c (Figure 6.). Furthermore, the existence of crystal modifications K' and K" is linked to the appearence of melting peaks at lower resp. higher temperatures than T_m, the modification with the lower melting point T_{m1} being a metastable one (Table I, Figure 8).

The fact that these phenomena are observed only for compound 4 leads to the assumption that they are related to the existence of a certain number of carbon atoms in the side chains. A similar effect is known for macromolecules with pendent n-alkyl groups, showing side chain crystallization only above a minimum side chain length of 10 to 12[16] in other cases 12 to 13[17] carbon atoms.

5. EXPERIMENTAL

General synthetic procedure

To a solution of $6{,}7 \cdot 10^{-3}$ mol cyanuric chloride (Aldrich) in 50 ml toluene was dropped a solution of $4 \cdot 10^{-2}$ mol of the appropriate dialkylamine (Aldrich, Riedel, Kodak) in 100 ml toluene. The reaction mixture was heated to 110°C for 12 hours under stirring. After cooling to room temperature the amine hydrochloride was filtered off and the toluene evaporated. The residue was repeatedly recrystallized.

The IR spectra (KBr) of compounds 1–4 show absorption bands at 1540, 1420, 1335–1320 and 810–800 cm^{-1}, typical of the s-triazine ring.[18] Further bands are 2930–2920, 2855–2850 (ν_{CH_2}), 1470 (δ_{CH_2} as), 1380–1375 (δ_{CH_2}sy) and 725–715 cm^{-1} (γ_{CH_2} rocking).

An additional band at 1220 cm^{-1} (γ_{CH_3}) is observed for 1. For compound 5 some bands are slightly shifted: 1570, 1423 cm^{-1} (ar, triazine), 1478 (δ_{CH_2} as).

1: 62% yield, colourless crystals (EtOH/MeOH 3:2 by vol., 2-fold recryst.)

MS m/e (%): 462(M^+,36), 447(10), 419(90), 405(8), 377(4), 363(100), 57(39).

^{1}H NMR ($CDCl_3$): δ = 0,88 (d,J = 6.8 Hz,—CH_3,6H), 2.16 (m,>CH—,1H), 3.30(d,J = 6.8 Hz,—CH_2—,2H), intensity ratio 6:1.04:2.06;

2: 35% yield, white needles (EtOH, recryst. temp.: 6°C, 3-fold recryst.)

MS m/e (%): 799(MH$^+$,100), 784(3), 770(11), 756(12), 742(12), 728(13), 714(40), 701(35), 700(30), 687(36), 686(30), etc.

^{1}H NMR ($CDCl_3$): δ = 0.88(t,—CH_3, 3H), 1.28(—CH_2—,10H), 1.57(m, β-CH_2,—2H), 3.43(t, α-CH_2—,2H), intensity ratio: 3.2:10:2.1:2;

3: 43% yield, white needles (EtOH, recryst. temp.: 6°C, 3-fold recryst.)

MS m/e (%): 967(MH$^+$,100), 952(3), 938(6), 924(6), 910(7), 896(6), 882(6), 868(6), 854(18), 841(23), 840(22), 827(18), 826(16), etc.;

^{1}H NMR ($CDCl_3$): δ = 0.88(t,—CH_3,3H), 1.27(—CH_2—,14H), 1.57(m,β-CH_2—,2H), 3.42(t, α-CH_2—,2H), intensity ratio 3.1:14:2:2.14;

$C_{63}H_{126}N_6$ Calc.: C 78.19; H 13.12; N 8.69
Found: C 78.17; H 13.26; N 8.80

4: 40% yield, white powder (EtOH, 3-fold recryst.)

MS m/e (%): 1135(MH$^+$,100), 1120(4), 1106(8), 1092(10), 1078(13), 1064(12), 1050(12), 1036(11), 1022(11), 1008(11), 994(25), 981(28), 980(20), 967(20), 966(15), etc.;

^{1}H NMR ($CDCl_3$): δ = 0.88(t,—CH_3, 3H), 1.26(—CH_2—,18H), 1.57(m,β-CH_2—,2H), 3.42(t, α-CH_2—,2H), intensity ratio: 3.4:18.6:2.2:2

$C_{75}H_{150}N_6$ Calc.: C 79.29; H 13.31; N 7.40
Found: C 78.96; H 13.31; N 7.71

7: 24% yield, white powder (recryst. of 4 from EtOH, mother liquor: precipitation at 6°C gave a mixture of 4 and 7 (Figure 1); after being filtrated off this mixture pure 7 was precipitated at −30°C;

MS m/e (%): 818(MH$^+$,100), 803(6), 789(14), 783(MH$^+$-Cl, 22.5), 775(20), 761(23), 747(22), 733(20), 719(12), 718(22), 705(22), 691(26), 677(47), 664(52), 663(55), 650(21), 649(18), 607(42), 509(68) etc.;

^{1}H NMR ($CDCl_3$): δ = 0.88(t,—CH_3,3H), 1.26(—CH_2—,18H), 1.56(m,β-CH_2—,2H), 3.44(m, α-CH_2—,2H), intensity ratio: 3.2:17.9:2.2:2.0;

$C_{51}H_{100}N_5Cl$ Calc.: C 74.83; H 12.31; N 8.56; Cl 4.33
Found: C 75.00; H 12.17; N 8.54; Cl 4.41

METHODS OF INVESTIGATION

The thermal behaviour was investigated with a polarizing microscope (Leitz, Laborlux, 12-Pol) equipped with a hot stage (Mettler FP 82) and by differential scanning calorimetry (Perkin-Elmer, DSC 7C). IR spectra were recorded on a Philips/Pye Unicam SP3-300, ^{1}H NMR spectra on a Bruker WM 250 spectrometer. Mass spectra were obtained with a Varian 312 mass spectrometer. GPC was performed by means of a Waters model ALC 200 with RI detector (Melz LCD 201) and two 0.5 m PL-gel columns (Polymer Laboratories, 5 μm particle diameter, 10 and 20 nm pore width), eluent THF, elution rate 0.5 ml/min.

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