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Isocyanatocyanates and (Iso)cyanatocyanurates Synthesis and Liquid Crystal Thermosets

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Summary: Synthesis and liquid crystal properties of a series of trifunctional star-shaped cyanurate rings containing mesogens with trimethylsiloxy-, hydroxy, cyanate- and isocyanate groups and of 4-cyanatophenyl-4-isocyanato benzoate **(2)** are described. Urethanes from the isocyanato-cyanurate **(8)** and monoalkohols were high-melting monotropic or non-lc-compounds. Cyclotrimerisation of the cyanuratocyanate **(7)** in comparison to the parent dicyanate **(1)** was studied to prove that the strong increase of isotropisation temperature with conversion was related to the polymer effect and not to the gel point. Cyclotrimerisation of **8** and of the isocyanatocyanate **(2)** give networks with identical structure of alternating cyanurate and isocyanurate cross-links, the former with nematic organisation, the latter isotropic, which proves the possibility of kinetic stabilization of a mesophase.

Introduction

Liquid crystal thermosets (LCT) from mesogenic dicyanates have been studied mainly in our laboratory[1] and by Ober's group.[2] LCT have no advantage over conventional thermosets in terms of modulus or coefficient of thermal expansion because they are macroscopically isotropic. Their applications are mostly based on optical properties or on the selective reflection of oriented chiral nematic films displaying color without dyes.[3-5] Cyclotrimerization of cyanates is a clean reaction which gives cyanurates (triazines) practically free of side-products thus allowing to study properties in relation to conversion or to gelation. We have synthesized a number of different diaromatic and triaromatic mesogenic dicyanates and studied their networks.[6,7] Thus we have reported the influence of catalysis on the maximum reaction temperature at which LCT are obtained, the isotropisation and the glass transition temperature as a function of conversion and in relation to the gel point.[7] One of the striking observations was the strong increase of the clearing temperature with conversion near to the gel point. The corresponding diisocyanates give isotropic networks without liquid crystal organization. To decide whether the gel point has an influence on the liquid crystalline (lc)-properties we were interested in a "monomer" giving a network with the same chemical structure

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but different critical conversion. The present paper deals with the synthesis of star shaped trifunctional cyanurato mesogens with different functional groups (Tab. 1) and of 4-isocyanatophenyl 4-cyanatobenzoate and the formation of thermosets from cyanate and isocyanate mesogens.

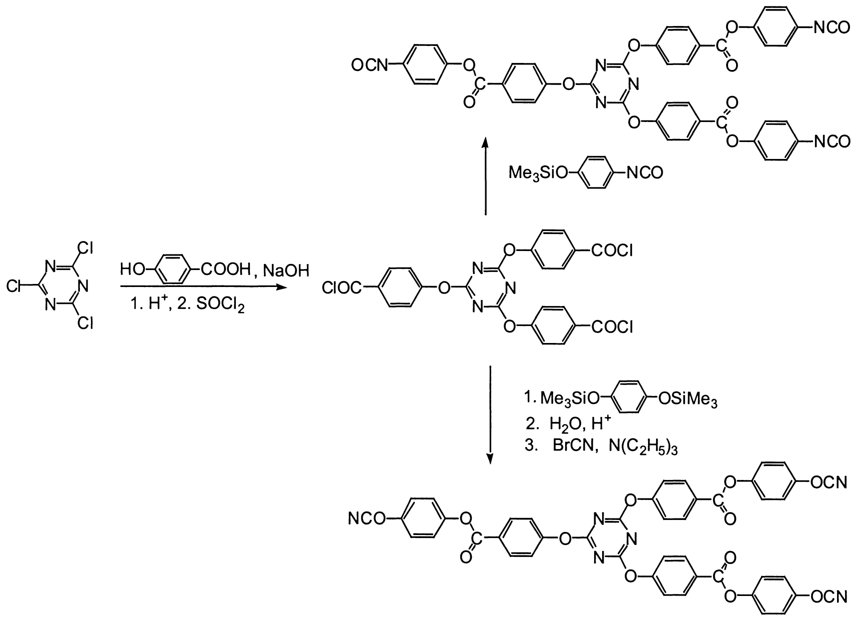
Results and discussion

Synthesis

The aim in the synthesis of the cyanurate based trifunctional mesogens was to have a general route in a multi-step reaction sequence which allowed to use intermediates for the synthesis of specifically functionalized monomers. Starting point was cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) which was reacted with 4-hydroxy benzoic acid to yield 2,4,6-tris(4-carboxyphenoxy)-1,3,5-triazine as a colorless high melting solid (m.p. 319 °C). Reaction of this triacid with thionyl chloride in boiling chlorobenzene gave the corresponding acid chloride 2,4,6-tris(4-chlorocarbonylphenoxy)-1,3,5-triazine (**4**) the key intermediate for the following reactions.

Esterification of **4** was made with excess 1,4-bis(trimethylsiloxy)-benzene in boiling o-dichlorobenzene using some crystals of hydroquinone as catalyst.[8,9] Chlorotrimethylsilane formed during the reaction was distilled off. After removal of solvents and excess 1,4-bis(trimethylsiloxy)-benzene 2,4,6-tris[4-(4-trimethylsiloxyphenoxycarbonyl)-phenoxy]-1,3,5-triazin (**5**) was obtained in almost quantitative yield as a brownish solid. Desilylation of **5** was achieved by dissolving in a mixture of acetone, water and a few drops of dilute hydrochloric acid at room temperature until the characteristic IR-bands of the siloxy groups had disappeared. 2,4,6-tris[4-(4-hydroxyphenoxycarbonyl)-phenoxy]-1,3,5-triazine (**6**) was obtained in 88 % yield (m.p. 250 °C).

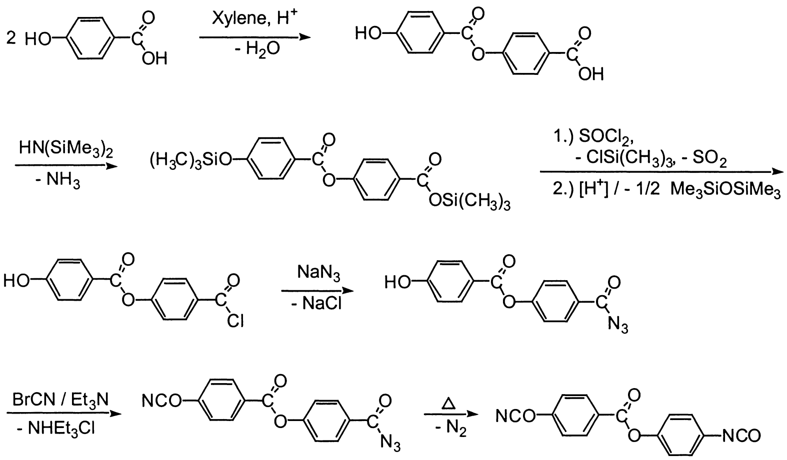
The trifunctional cyanate 2,4,6-tris[4-(4-cyanatophenoxycarbonyl)-phenoxy]-1,3,5-triazine (**7**) was made from **6** with cyanogen bromide and triethylamine in acetone.[10] Residual phenolic compounds were removed by purification with flash chromatography. The yield of pure **7** was 35 %. The reaction sequence leading from cyanuric chloride to the siloxy, hydroxy and cyanate mesogens is shown in Scheme 1.



Scheme 1

The trifunctional isocyanate 2,4,6-tris[4-(4-isocyanatophenoxycarbonyl)-phenoxy]-1,3,5-triazine (**8**) was synthesised from **4** adopting a procedure which has been used previously to synthesise liquid crystalline diaromatic and triaromatic ester group containing diisocyanates.[8] Unlike the free hydroxy group the silyl protected phenolic group does not react with the isocyanate group. The conditions of the reaction between **4** and 4-trimethylsiloxyphenylisocyanate were similar to those applied for the synthesis of **5** except that sulfuric acid was used as catalyst. **8** was obtained in 48 % yield (m.p. 164 °C).

The synthesis of 4-isocyanatophenyl 4-cyanatobenzoate (**2**) started from 4-hydroxybenzoic acid which was converted into the dimer 4-(4-hydroxybenzoyloxy)-benzoic acid through azeotropic esterification in xylene. The dimer contained small amounts of monomer and oligomers, hence it was silylated with hexamethyldisilazane and purified by distillation to give the pure dimer after desilylation in 74 % yield compared to 32 % in known procedures which in addition require protecting group chemistry.[11,12]



Scheme 2

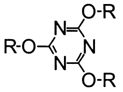
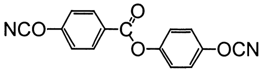
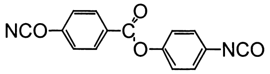
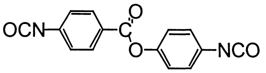
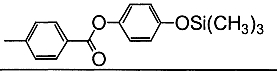
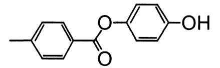
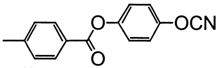
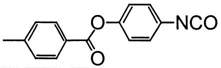
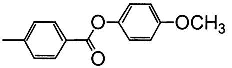
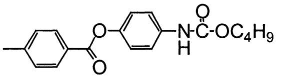
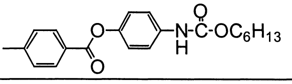
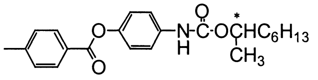
Following a procedure reported by Kricheldorf[13] 4-(4-trimethylsiloxybenzoyloxy)-trimethylsilyl benzoate was reacted with thionyl chloride and the trimethylsiloxy group was hydrolysed by trituration of the ether solution with water. This solution was reacted with aqueous sodium azide to give 4-(4-hydroxybenzoyloxy)-benzoyl azide (**16a**) in 88 % yield. The azide upon reaction with cyanogen bromide in acetone yielded 4-(4-cyanatobenzoyloxy)-benzoyl azide which in boiling cyclohexane underwent a Curtius-rearrangement to 4-isocyanatophenyl 4-cyanatobenzoate (**2**).

All new intermediates and products were characterized by IR-, NMR-spectroscopy and elemental analysis.

Liquid crystal properties

All cyanurate ring containing compounds with the phenyl benzoate moieties attached are mesogenic,[6] therefore they were investigated by polarized light microscopy and thermal analysis. As the mesogenic core is identical for all cyanurates this gives also information about the ability of the functional groups to stabilize a mesophase. The results are summarized in Table 1. All cyanurate mesogens form a nematic mesophase either monotropic or enantiotropic. The clearing point increases in the order cyanate < trimethylsiloxy < methoxy ≈ hydroxy < isocyanate. The trimethylsiloxy compound (**5**) is glassy with a TG of 78 °C while the other compounds are crystalline solids. Cyanurato cyanate (**7**) and -isocyanate (**8**) melt at approximately 160 °C while the hydroxy compound (**6**) has the highest melting point with 250 °C. The intermediates as well as the isocyanate and cyanate can be used as mesogenic building blocks for a variety of lc-polymers.

Table 1. Structure and mesogenic properties of monomers and intermediates.

No.	**Monomer** or **R** 	**Tm** [°C]	**LC phase**	**Ti** [°C]
1		139	(n	32[a])
2		118	n	148
3		113	(n	84)
5		78 (Tg)	n	174
6		250	(n	243)
7		156	(n	143)
8		164	n	280
9		200	n	239
11		240	(n	221)
12		210	(n	195)
13		220	i	

The phenyl benzoates with cyanate and isocyanate functional groups are also nematic liquid crystalline compounds. Starting from the dicyanate (**1**) the clearing point increases by approximately 60 °C if a cyanate group is replaced by an isocyanate group (**2** and **3**). This reflects the higher mesogenic potential of the isocyanate group with respect to the isomeric cyanate group.

The isocyanatocyanurate **8** was reacted with n-butanol, n-hexanol, and 2-octanol to elucidate whether polyurethane networks with liquid crystal organization could be obtained. Structures and mesogenic properties of the urethanes are included in tab. 1. The melting point increases significantly to 210 °C and more, while the clearing point is lowerd from 280 to 220 (**11**) and 195 °C (**12**) respectively. Clearing transitions can be observed only in the cooling mode (monotropic nematic phases). Cyanurato urethane **13** with a chiral alkohol should give a cholesteric mesophase, which would be quite interesting in an oriented state because of wavelength selective reflection of light. This can be used for paints without dyes or pigments.[3] Unfortunately **13** does not give a mesophase in an accessible temperature range, in addition crystallization would destroy the mesophase as well as the orientation.

Thermosets

Cyclotrimerisation of the dicyanate **1** has been reported in previous papers.[7] Main results were that the two cyanate groups have different reactivity i.e. that the cyanate at the acid ring (A-group) ist 6.3 times more reactive than the cyanate moiety attached to the phenol part of the molecule (B-group). As a consequence the critical conversion at which gelation occurs is not at 50 % as is the case for isoreactive functional groups but at 62 %. From studies on model cyanurates we know that the direction of the ester groups in cyanurates is of paramount influence on the mesogenic properties, i.e. no lc properties were observed if the cyanate group of the phenol part of the molecule was transformed into the cyanurate.[6]

Cyclotrimerisation of dicyanatophenyl benzoate should reflect these features. Modelling the distribution of different mono-cyanurates as a function of conversion shows that predominantly the trimer BBB is formed (27 % at 40 % conversion) followed by ABB with 7 % while the other isomers can be neglected. Only 4 % of higher oligomers have been formed at 40 % conversion. The distribution of the four possible monocyanurates as a function of conversion is shown in Figure 1 together with the structure of the two main isomers.

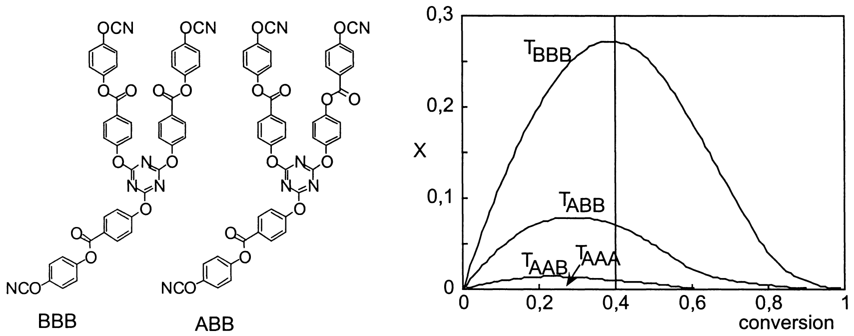


Figure 1. Structure and distribution of monocyanurates vs. conversion.

The predominant formation of the BBB-cyanurate with the relatively high clearing point suggests that beyound 50 % conversion mostly cyanurate rings will be formed from B-groups which have the unfavourable direction of ester groups. This is indeed what happens as shown in Figure 2 where the clearing point (Ti) of the cyclotrimerisation of **1** is shown as a function of conversion. Experimentally a sample of **1** was cyclotrimerized in a flask under argon at 160 °C; samples were taken by dipping a glass rod in the mixture and quenching liquid nitrogen. Conversion was determined by IR-spectroscopy, Tg from DSC, Ti by polarized light microscopy. First reliable data were obtained at conversion above 30 %. At lower conversion crystallization of **1** prevented determination of Ti. Up to 45 % conversion the clearing temperature increases almost proportional with conversion then a slight decrease is observed followed by a strong increase above 55 % conversion. Ti could be measured up to 62 % conversion (220 °C); at higher conversion (clearing temperature) additional reaction of cyanate groups gave uncontrollable increase of Ti.

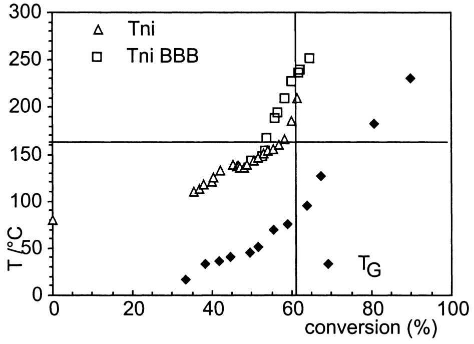
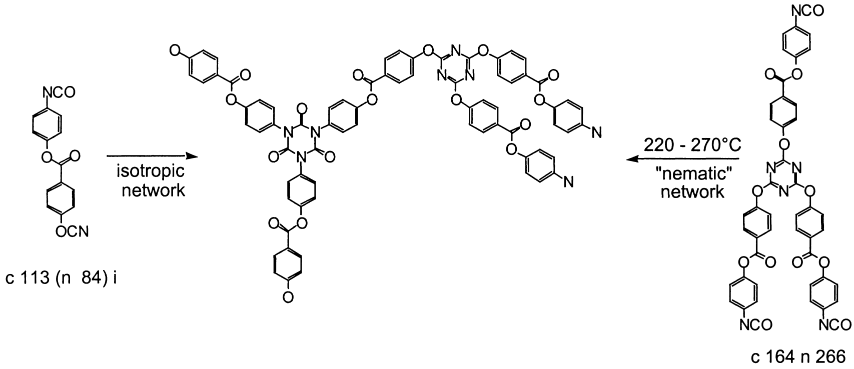


Figure 2. Isotropization and glass transition temperature vs. conversion for **1** (triangles) and **7** (open squares).

The gel point of a trifunctional cyanate where the functional groups have equal reactivity is at 33 % conversion. **7** corresponds to a dicyanate where all A-groups react before reaction of the first B-group, hence the gel point will be at 67 % conversion in Figure 2. A similar experiment for **7** is included in Figure 2. Initially there is almost no increase in clearing temperature because only infavourable structures are formed. A strong increase follows which reaches 230 °C at 60 % conversion well before the gel point. Obviously it is the polymer effect and not the gel point which is responsible of the strong increase of the clearing point.

Mesogenic diisocyanates without flexible spacers do not form LCT because of the rigid star-shaped isocyanurate ring as crosslink. Cyanurate moieties act as flexible elements due to rotational freedom of the C-O-C bridge.[6] Hence we studied the Cu^{II}-acetyl acetonate catalyzed cyclotrimerization of both the isocyanatocyanate (**2**) and the isocyanatocyanurate (**8**) which form a network containing alternating cyanurate and isocyanurate cross-links (Scheme 3). Under these conditions both functional groups react.



Scheme 3

No conditions were found under which an LCT was formed from **2** while cyclotrimerization of **8** gave a nematic LCT when reacted between 220 and 270 °C. Obviously the isotropic phase is thermodynamically stable, the nematic phase, however, is kinetically stabilized during polymerization. The higher rigidity of isocyanurate as compared to cyanurate rings shows from the final conversion which is 88 % for **8** and 95 % for **7**.

Trifunctional star-shaped cyanurato mesogens were synthesized and shown to be valuable building blocks for lc-polymers. Cyclotrimerization of the cyanuratocyanate **7** as compared to **2** proved that gelation has no influence on the clearing temperature of the reaction mixture. Kinetic stabilization allows to obtain a nematic LCT with alternating cyanurate and isocyanurate cross-links from **8** while isotropic thermoset networks with identical chemical structure are formed from **2**.

Acknowledgment

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