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Liquid Crystalline Thermosets through Cyclotrimerization of Diaromatic Dicyanates

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ABSTRACT: Two mesogenic dicyanates, 4-cyanatophenyl 4-cyanatobenzoate (**1**) and 4,4′-dicyanatobiphenyl (**2**), were synthesized and cyclotrimerized to form *s*-triazine thermoset networks. Networks with frozen nematic textures were obtained from **1**, and from mixtures of **1** with up to 50% of **2**, although pure **2** formed an isotropic network independent of curing conditions. The curing reaction was monitored by infrared spectroscopy and calorimetry. The final conversion of both rigid monomers was approximately 80% from dynamic DSC experiments. On isothermal curing of **1** at 160 °C, a liquid crystalline phase appeared after 57% conversion. The nematic/isotropic transition and the glass transition temperature of **1** was measured as a function of conversion. The maximum temperature at which anisotropic networks can be obtained on isothermal curing decreases from 240 to 150 °C with increasing reactivity (amount of catalyst) of the reacting system.

Introduction

Networks, in which a liquid crystalline organization is irreversibly fixed by a chemical reaction, also referred to as liquid crystal thermosets (LCT), have been reported by several groups, the first indeed prior to thermoplastic side-chain LCP.[1,2] The experimental results available to date have been discussed in a recent review by Ober.[3]

The Philips group with Broer, Hikmet, and others investigated the photopolymerization of bis(acrylates) with flexible spacers between the functional groups and the mesogen.[4−6] They related the structure of the monomers, and of the mesophase of the aligned networks in thin films produced by photopolymerization, to the anisotropy of physical properties of these films. Properties such as coefficient of thermal expansion, modulus of elasticity, and refractive index in macroscopically aligned networks were studied.[7,8] They also reported first applications of these systems.

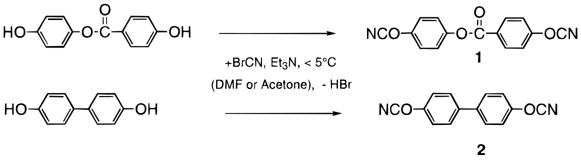
Ober and co-workers focused on amine cured epoxy and cyanurate LCT. They were able to obtain networks with either nematic or smectic organization from one mesogenic monomer, depending on the curing conditions.[9] Macroscopically oriented specimens were obtained in mechanical or magnetic fields, and the anisotropy of the coefficient of thermal expansion was reported. A similar study was published on cyanurate networks.[10] The systems used by Ober and his group were not ideal in terms of relating mesophase formation with the curing kinetics and network built up. The studies on cyanurate networks were made with a triad dicyanate containing three isomers with OCN groups of different reactivity in an unknown ratio, while several competing cross-linking reactions make this analysis extremely difficult in the case of epoxy/amine networks.

Monomers with suitable mesogenic properties, clean cross-linking reactions, and a precise spectroscopic method to follow the kinetics are required for a systematic study of these features. Cyanates seem to be ideally suited to study anisotropic networks, since cyclotrimerization, which can easily be followed by infrared spectroscopy, is the only cross-linking reaction taking place.[11] We initiated our systematic study of cyanate LCT with an investigation of the mesogenic properties of the cyanate group[12] and of the 2,4,6-tris(aryloxy)-1,3,5-triazine (cyanurate) moiety and showed that cyanates are poor mesogens but that cyanurate rings stabilize a mesophase.[13]

The work presented in this paper deals with the synthesis, characterization, and polycyclotrimerization of two diaromatic mesogenic dicyanates and the LC thermosets obtained therefrom.

Results and Discussion

Synthesis and Characterization of Monomers. The two dicyanates used in this study were 4-cyanatophenyl 4-cyanatobenzoate (**1**) and 4,4′-dicyanatobiphenyl (**2**). The former has been claimed in a patent but neither an experimental procedure nor any analytical data have been revealed.[14] The latter has been described before without allusion to potential mesogenic properties.[15,16] The cyanates were obtained from the reaction of the corresponding bis(phenols) with cyanogen bromide in the presence of triethylamine as an acid acceptor as shown in eq 1. 4-Hydroxyphenyl 4-hydroxybenzoate, which is also an intermediate for other mesogens, was synthesized from hydroquinone and 4-hydroxybenzoic acid by an acid-catalyzed esterification reaction[17] and 4,4′-dihydroxybiphenyl is commercially available.



(1)

Both cyanates were purified by recrystallization or flash chromatography in order to remove traces of catalytic impurities, e.g., phenols, which can cause polymerization at rather low temperatures. According to the heat flow in a differential scanning colorimetry (DSC) trace, a sample purified by flash chromatography does not react significantly up to 250 °C with a maximum at 320 °C. However, the phenol-catalyzed sample starts reacting almost immediately after melting with a maximum at 260 °C. In some cases, stirring the crude

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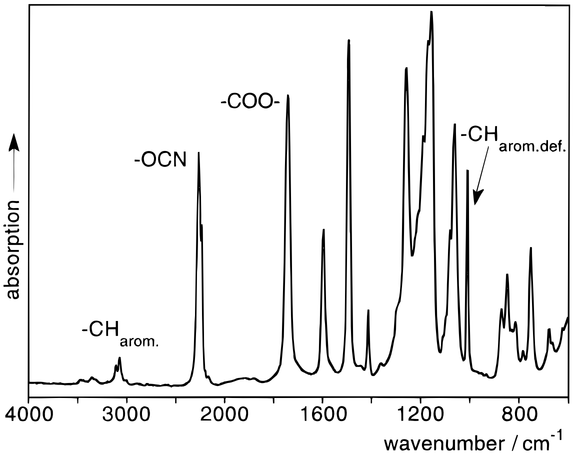


Figure 1. FTIR spectrum of 4-cyanatophenyl 4-cyanatobenzoate (**1**).

product with a liquid capable of dissolving the remaining traces of the phenol or the tertiary amine is sufficient to greatly increase monomer purity and to raise the onset temperature of cyclotrimerization.

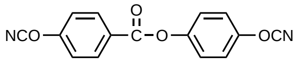
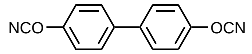
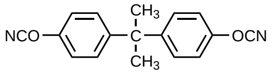
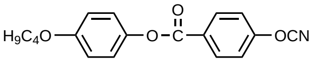
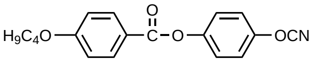
Monomers **1** and **2** were characterized by elemental analysis, infrared and NMR spectroscopy, and thermal analysis. The infrared spectrum of **1** is shown in Figure 1. It has the characteristic absorptions of the aromatic C−H stretching at 3100−3000 cm^{-1}, of the cyanate group at 2274 and 2232 cm^{-1}, of the ester carbonyl at 1731 cm^{-1}, of the aromatic ring vibration at 1598 and 1505 cm^{-1}, and of the *para*-substituted aromatic out-of-plane deformation vibration at 1012 cm^{-1}.

The proton NMR spectra of the two cyanates are rather simple and show the expected absorptions. **1** has two AA′XX′ systems, one at 7.38 ppm, which is not fully resolved, and the other at 7.48 and 8.33 ppm with a coupling constant of 14.1 Hz. This reflects the electronic properties of the oxycarbonyl and the carbonyloxy groups attached to the two phenyl rings (benzoyl and phenol), which cause a difference in reactivity of the cyanate groups attached to either ring. The biphenyl derivative **2** shows two identical nonresolved AA′XX′ systems at 7.40 and 7.65 ppm with coupling constants of 7.3 Hz.

Cyclotrimerization of Dicyanates. The monomers were cyclotrimerized either thermally without additional catalyst or in the presence of small amounts of the corresponding phenol or of Cu(II)−acetylacetonate.[18] Homogeneous samples for kinetic investigations were prepared by dissolving the cyanate and the catalyst in benzene and freeze-drying. The reactions were followed by infrared spectroscopy, by dynamic or isothermal DSC, and by polarized light microscopy.

DSC has been frequently used to determine the kinetics, the conversion, and the glass transition temperature of partially cured thermosets.[19,20] There is contradictory information on the enthalpy of cyclotrimerization ranging from −88.7 [20] to −118.8 kJ/mol,[18] sometimes with rather large error margins: −97.3 ± 13.9 kJ/mol.[21] Therefore, we determined the reaction enthalpies of two monocyanates described in a previous paper,[12] of 2,2-bis(4-cyanatophenyl)propane, and of monomers **1** and **2**. The data are shown in Table 1. Identical results with heating rates from 5 to 20 K/min were obtained for the monofunctional compounds if care was taken to ensure that no weight loss had occurred during the measurement (closed DSC pan).

Table 1. Enthalpy of Cyclotrimerization and Final Conversion of Mono- and Dicyanates

cyanate	$\lvert\Delta H_R\rvert$ (kJ/mol of OCN)	conversn (%)
(1) 	88.6 ± 0.80	79
(2) 	90.6 ± 0.75	80
	113.8 ± 0.62	99
	115.0 ± 1.8	100
	114.0 ± 1.8	100

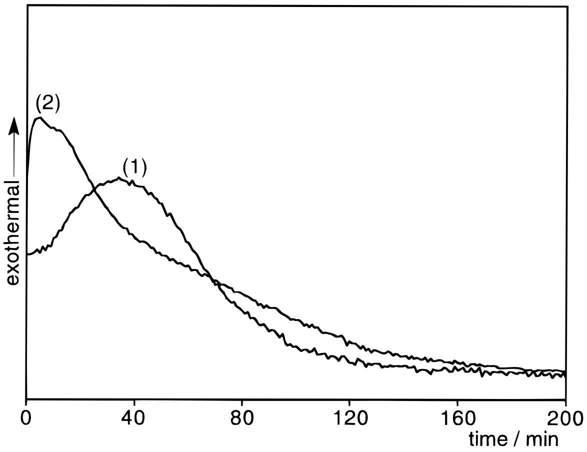


Figure 2. Isothermal (DSC) curing of **1** with different amounts of Cu(acac)$_2$ catalyst: (1) 0.2 and (2) 0.3 mol %.

The value obtained for the two monocyanates is −114.5 kJ/mol OCN. Based on this enthalpy, the final conversion of the 2,2-bis(4-cyanatophenyl)propane in a dynamic DSC scan is greater than 99% while the more rigid mesogenic dicyanates (**1**, **2**) have a final conversion of 79 and 80% (cf. Table 1). The high final conversion of the commercial dicyanate has its origin in the relatively high flexibility of this monomer, which is caused by rotation around the tetrahedral carbon between the two aromatic rings or by ring flipping. The mesogenic dicyanates have a more rigid structure, which prevents the cyanate groups from finding each other at lower conversion. Vitrification, which can be responsible for a decrease in reaction rate particularly in isothermal curing, should not be the main reason for such a decrease in a dynamic cure cycle. Complete conversion of the cyanate groups of **1** could be achieved after postcuring at 230 °C for 10 h, 250 °C for 2 h, and heating to 350 °C at a rate of 10 K/min.

Isothermal curing at 145 °C was also followed by DSC with different amounts of catalyst as shown in Figure 2. After 2−3 h, the reaction almost ceases because of vitrification. The conversion that can be reached at this temperature is 71%. A dynamic scan of the partially cured thermoset with a heating rate of 20 K/min reveals a glass transition temperature of 150 °C and an additional heat of reaction between 9 and 10 kJ/mol, which adds to a final conversion of about 80%. This is identical with the reaction enthalpy found in dynamic curing within experimental error.

Conversion of cyanate groups was monitored by FTIR spectroscopy, a method that has been used by several groups before.[10,11,20,22] The characteristic CN absorption in the range from 2200 to 2300 cm^{-1} has been chosen

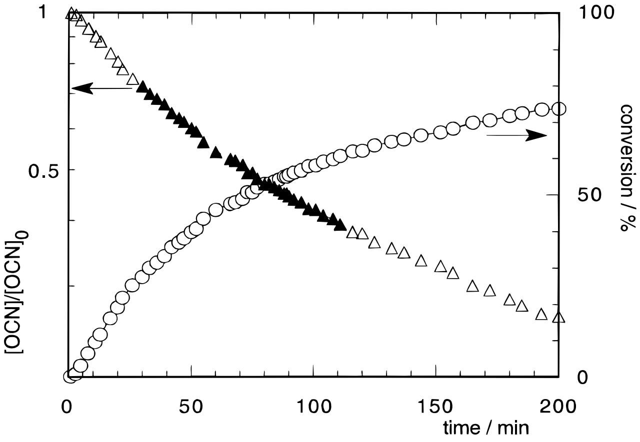


Figure 3. Conversion/time and first-order plot of the cyclotrimerization of **1** at 160 °C.

throughout to monitor consumption of cyanate groups. Different bands, however, have been used for internal calibration. A band that proved to be independent of conversion yet with a reasonable intensity is the aromatic deformation vibration at 1022−996 cm^{-1}. This absorption has been used by Papathomas[22] and was also taken as internal standard for the kinetic investigation of the cyclotrimerization reaction in this study. The C−H stretching absorptions are too weak for this use in fully aromatic cyanates (cf. Figure 1).

A clean first-order reaction was found for the commercial 2,2-bis(4-cyanatophenyl)propane in agreement with similar results of Bauer et al.[23,24] The cyclotrimerization of **1**, however, cannot be described by first-order kinetics up to high conversion. A time/conversion plot together with a first-order plot of this reaction is shown in Figure 3. Since a catalytic effect of the ester group is rather unlikely, a possible explanation is a difference in reactivity of the two cyanate groups in **1**. As suggested by the NMR spectrum, the electronic properties of the two 1,4-disubstituted aromatic rings are different. The OCN group attached to the benzoyl part should be more prone to a nucleophilic attack because of the electron-withdrawing effect of the oxycarbonyl group. The other OCN group should be less reactive because is in conjugation with the phenol oxygen, a substituent with electron-donating properties.

If one accepts the unequal reactivity of the two cyanate moieties in **1**, it is reasonable to argue that in the beginning of the cyclotrimerization the more reactive groups react almost exclusively, while in the final stage these have disappeared and only the remaining less reactive groups undergo cyclotrimerization. Hence, both parts of the curve symbolized by open triangles were treated by first-order kinetics. Rate constants obtained were $k_A = 0.024$ min^{-1} and $k_B = 0.0034$ min^{-1}, with correlation coefficients of 0.999 for the low-conversion part and 0.997 for the high-conversion part. A 7-fold higher reactivity of the A group with respect to the B group is found from the ratio of the two rate constants.

Attempts to prove the different reactivity of the two cyanate groups of **1** by ^{13}C-NMR spectroscopy in analogy to the work reported on 2,2-bis(4-cyanatophenyl)propane have not been successful.[25] Adopting the conditions and parameters used by Fang did not allow us to obtain quantitative information.

Mesomorphic Properties of Polycyanurate Networks. Cyclotrimerization was followed by polarized light microscopy on a hot stage. Curing of monomer **1** started in an isotropic melt. After some time, nematic droplets appeared and coalesced soon; the texture remained even if the temperature was raised to 330 °C, the maximum temperature of the hot stage used. The sample then was insoluble, and the texture was stable over the whole temperature range up to the decomposition of the material. Figure 4 shows the birefringent textures of a cured sample of **1**. Only isotropic networks were obtained from monomer **2** regardless of which curing conditions were applied. Mixtures of monomers **1** and **2** were prepared by freeze-drying benzene solutions. A phase diagram is shown in Figure 5. A eutectic is found for equimolar amounts of **1** and **2** with a melting point of 109 °C, which is almost 30 °C lower than those of the pure monomers. When these mixtures were polymerized at 160 °C without added catalyst, anisotropic networks were obtained from an initially isotropic melt if the content of **1** was above 40 mol %. These mixtures have the advantage that they can be processed at lower temperature because of the melting point depression.

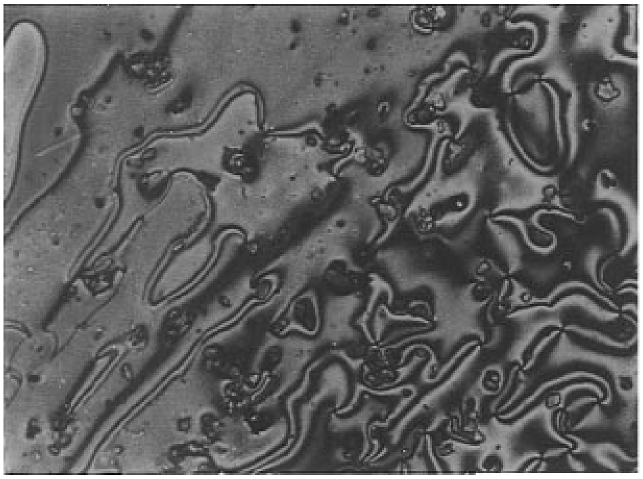


Figure 4. Nematic texture of cyanurate network from **1** (reproduced at 95% of original magnification).

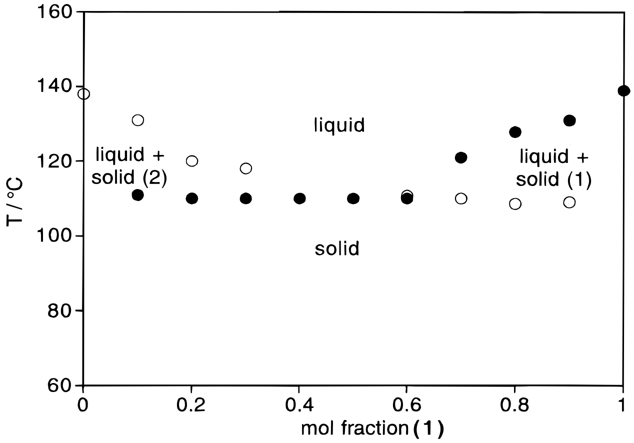


Figure 5. Phase diagram of monomers **1** and **2**.

Isotropic thermoset networks were obtained from mixtures of **1** and 2,2-bis(4-cyanatophenyl)propane already with 5 mol % of the latter. This seems to rule out the possibility of reducing the cost of the material by blending a mesogenic diaromatic with commercially available nonmesogenic dicyanates.

The conversion at which the isotropic/nematic transition takes place could also be monitored by FTIR spectroscopy in a kinetic experiment if a suitable film thickness was chosen. Since nematic solutions or melts are turbid and isotropic melts are transparent, the

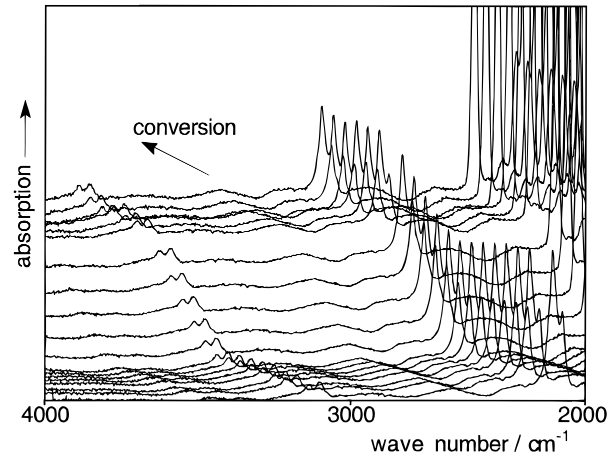


Figure 6. Isotropic/nematic transition observed as increased absorbance in the infrared spectra during polycyclotrimerization of **1**.

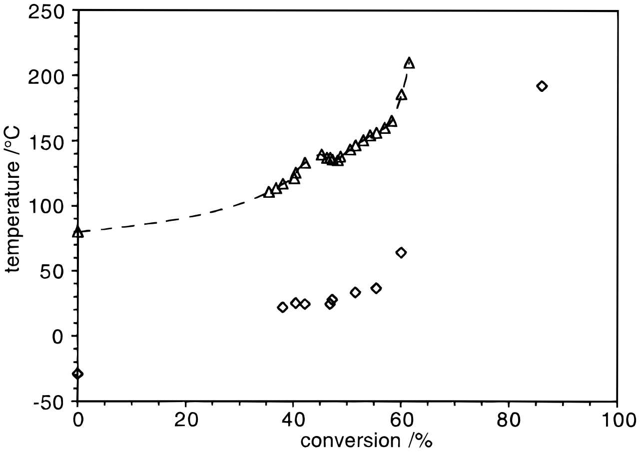


Figure 7. Nematic/isotropic transition (triangles) and glass transition temperature (squares) as a function of conversion observed during polycyclotrimerization of **1** at 160 °C.

scattering of light in the nematic melt results in an apparent increase in absorption, which is shown in Figure 6. In the case of noncatalyzed polycyclotrimerization of monomer **1** at 160 °C, the isotropic/nematic transition occurs between 57 and 59% conversion of cyanate groups. Isothermal curing of monomer **1** was made at temperatures between 140 and 230 °C. At 230 °C, no liquid crystalline phase was observed in the resulting network. On the other hand, once nematic textures had appeared, the temperature could be raised in the hot stage without any indication of isotropization.

The clearing point as a function of conversion was measured during the polycyclotrimerization of 4-cyanatophenyl 4-cyanatobenzoate. The reaction was carried out at 160 °C in bulk in an argon atmosphere. Aliquots were removed with a glass rod, quenched in liquid nitrogen, and stored in a freezer. They were investigated by IR spectroscopy for conversion, by DSC for the glass transition temperature and clearing point, and by polarized light microscopy for clearing transitions and identification of the mesophase. The results are shown in Figure 7. The clearing point increases from 80 °C, which is the virtual clearing point of the monomer, to approximately 120 °C at 50% conversion. Between 45 and 50% conversion the clearing point decreases, goes through a minimum, and increases then from 160 to 220 °C in a conversion interval of less than 10% (58−65%).

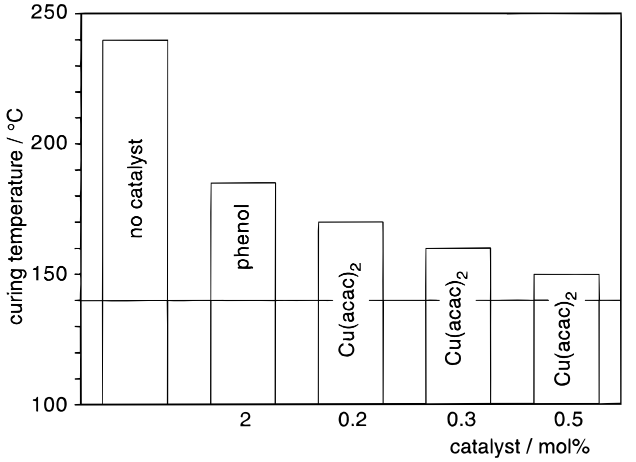
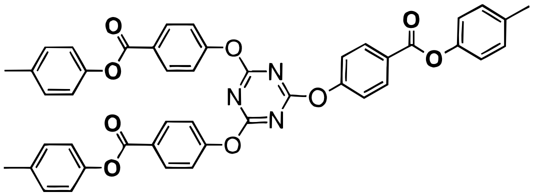
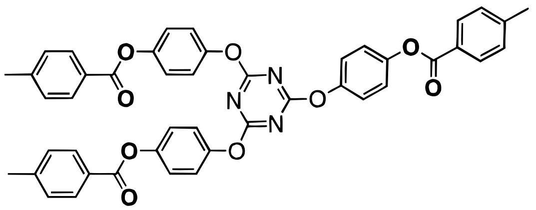


Figure 8. Maximum temperature for the occurrence of birefringent textures in triazine networks from **1** as a function of curing rate (catalysis).

A qualitative explanation of this behavior can be given on the basis of the different reactivities of the two cyanate groups in **1** and on the basis of the influence of the direction of the ester group on the mesogenic properties. As previously reported the cyanurate obtained from 4-butoxyphenyl 4-cyanatobenzoate (**3a**) has



3a



3b

an enantiotropic mesophase whereas that from the isomeric 4-cyanatophenyl 4-butoxybenzoate (**3b**) is isotropic.[13] Due to the higher reactivity of the cyanate group attached to the benzoyl ring, cyclotrimers with the favorable structure **3a** are predominantly formed in the initial stage of the cyclotrimerization while the non liquid crystalline cyanurate structures occur in the later state of network formation, giving rise to a decrease in the clearing temperature. The strong rise that follows is linked to the formation of high molecular weight structures since the system is close to or beyond the gel point at this stage.

The maximum temperature at which an anisotropic network can be obtained depends on the amount of catalyst used in the cyclotrimerization of **1**. In Figure 8, the maximum temperatures are plotted against the reactivity of the curing system. This temperature decreases with increasing reactivity, thus limiting the temperature range in which anisotropic networks can be obtained. Increasing reactivity decreases selectivity; hence increasingly larger amounts of cyanurate oligomers with lower clearing points or non liquid crystalline properties are formed.

Consideration of the phase behavior of cyanate and cyanurate requires that the clearing transition of the branching or cross-linking mixture of **1** increases with increasing conversion and reaches the curing temperature at one point during thermoset formation. Kinetics of the isotropic/nematic transition require the formation of a liquid crystalline phase to occur before the cross-link density reaches a certain value and before the glass transition temperature of the system reaches the curing temperature. To what extent the latter phenomena play a role will be investigated in a forthcoming paper.

Conclusions

Anisotropic thermoset networks were obtained by polycyclotrimerization of 4-cyanatophenyl 4-cyanatobenzoate, which begins in the isotropic phase. Conversion of cyanate groups was followed by FTIR spectroscopy, and the isotropic/nematic transition could be correlated with conversion. A maximum and a minimum was found for this transition which could be explained by the relative amounts of different triazines as a consequence of the nonsymmetrical structure of monomer **1**. An influence of catalysis on the maximum temperature at which anisotropic networks can be obtained has been observed. A detailed kinetic analysis and a correlation of the glass transition temperature with conversion and isotropic/nematic transition is under way.

Experimental Section

Materials. 4-Hydroxyphenyl 4-hydroxybenzoate was synthesized as described in ref 17. Flash chromatography was performed on Merck silica gel 60/ 40-63 with chloroform as eluent. Complete conversion of **1** to the cyclotrimer was achieved by postcuring at 230 °C for 10 h, 250 °C for 2 h, and heating from 250 to 350 °C at a rate of 10 K/min.

Methods of Characterization. Infrared spectra were recorded on a Bruker IFS48-FTIR spectrometer as films between NaCl plates. Solid samples were either dissolved in an appropriate solvent, prepared as Nujol mulls, or measured in a Bruker FTIR microscope A590. NMR spectra were made on a Bruker AC-200 using deuteriochloroform with TMS as internal standard. Thermal transitions were investigated with a Nikon Optiphot 2 polarizing microscope equipped with a Mettler FP 82 hot stage and FP 80 processing unit. Transition enthalpies and temperatures were recorded with a Mettler DSC/30 TC 11 system (heating rate was 20 K/min).

Elemental analyses were made by Mikroanalytisches Labor Beller, Göttingen, Germany.

Cyanate Esters. To a stirred solution of 0.05 mol of the bis(phenol) and 0.105 mol of cyanogen bromide dissolved in 200 mL of anhydrous dimethylformamide or acetone was added 0.10 mol of triethylamine dropwise during 30 min, keeping the temperature between 0 and 5 °C. After the addition was complete, the reaction mixture was stirred for 10 min at 0−5 °C and poured on ice/water. The precipitate that formed was filtered off, washed with water, and dried in vacuo. The crude product was stirred with 2-propanol, purified by flash chromatography, and recrystallized from acetone or toluene.

4-Cyanatophenyl 4-Cyanatobenzoate (1). Yield: 11.1 g, 60.6%. T_m: 139 °C. IR (Nujol): 2274, 2232 (CN),1731 (C=O), 1590 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$/TMS): δ 7.38 (m, 4H), 7.48 (d, $^3J = 14.1$ Hz, 2H), 8.33 ppm (d, $^3J = 9.2$ Hz, 2H). Anal. Calcd for $C_{15}H_8O_4N_2$ (280.24): C, 64.3; H, 2.9; N, 10.0. Found: C, 64.5; H, 3.0; N, 9.9.

4,4′-Dicyanatobiphenyl (2). Yield: 8.14 g, 69.5%. T_m: 138−139 °C (lit.[16,26] 138 °C). IR (Nujol): 2270, 2236 (CN), 1590 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$/TMS): δ 7.40 (d, $^3J = 7.3$ Hz, 4H), 7.65 ppm (d, $^3J = 7.3$ Hz, 4H). Anal. Calcd for $C_{14}H_8O_2N_2$ (236.23): C, 71.2; H, 3.4; N, 11.9. Found: C, 71.1; H, 3.5; N, 11.9.

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References and Notes

(1) Strzelecki, L.; Liebert, L. *Bull. Soc. Chim. Fr.* **1973**, 597.
(2) Clough, S. B.; Blumstein, A.; Hsu, E. C. *Macromolecules* **1976**, *9*, 123.
(3) Barclay, G. G.; Ober, C. K. *Prog. Polym. Sci.* **1993**, *18*, 899.
(4) Broer, D. J.; Gossink, R. G.; Hikmet, R. A. M. *Angew. Makromol. Chem.* **1990**, *183*, 45.
(5) Hikmet, R. A. M.; Lub, J.; Broer, D. J. *Adv. Mater.* **1991**, *3*, 392.
(6) Hikmet, R. A. M.; Lub, J.; Maassen, v. d. B. P. *Macromolecules* **1992**, *25*, 4194.
(7) Broer, D. J.; Finkelmann, H.; Kondo, K. *Makromol. Chem.* **1988**, *189*, 185.
(8) Broer, D. J.; Hikmet, R. A. M.; Challa, G. *Makromol. Chem.* **1989**, *190*, 3201.
(9) Barclay, G. G.; Ober, C. K.; Papathomas, K. I.; Wang, D. W. *J. Polym. Sci., Polym. Ed.* **1992**, *30*, 1831.
(10) Barclay, G. G.; Ober, C. K.; Papathomas, K. I.; Wang, D. W. *Macromolecules* **1992**, *25*, 2947.
(11) Bauer, M.; Bauer, J.; Kühn, G. *Acta Polym.* **1986**, *37*, 218.
(12) Mormann, W.; Zimmermann, J. G. *Liq. Cryst.* **1995**, *19*, 227.
(13) Mormann, W.; Zimmermann, J. G. *Liq. Cryst.* **1995**, *19*, 481.
(14) Hefner, R. E., Jr.; Earls, J. D.; Puckett, P. M. EP 409 069, 1991; *Chem. Abstr.* **1991**, *115*, 93 211a.
(15) Grigat, E.; Pütter, R. *Chem. Ber.* **1964**, *97*, 3012.
(16) Vohwinkel, E.; Baese, H.-J. *Chem. Ber.* **1974**, *107*, 1213.
(17) Müller, H. P.; Gipp, R. EP 0 252 357, 1987; *Chem. Abstr.* **1988**, *108*, 131 303.
(18) Bonetskaya, A. K.; Ivanov, V. V.; Kravchenko, M. A.; Pankratov, V. A.; Frenkel, T. M.; Korshak, V. V.; Vinogradova, S. V. *Polym. Sci. USSR* **1980**, *22*, 845.
(19) Simon, S. L.; Gillham, J. K. *Polym. Mater. Sci. Eng.* **1992**, *66*, 453.
(20) Simon, S. L. Ph.D. Thesis, Princeton University, Princeton, NJ, 1992.
(21) Gupta, A. M.; Macosko, C. W. *Macromolecules* **1993**, *26*, 2455.
(22) Papathomas, K. I. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30*, 158.
(23) Bauer, M.; Bauer, J.; Garske, B. *Acta Polym.* **1986**, *37*, 604.
(24) Bauer, M.; Bauer, J. *Makromol. Chem., Macromol. Symp.* **1989**, *30*, 1.
(25) Fang, T. *Macromolecules* **1990**, *23*, 4553.
(26) Grigat, E.; Pütter, R. DP 1 195 764, 1963; *Chem. Abstr.* **1965**, *63*, 16 276g.

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