Liquid crystalline Schiff bases with cyanate terminals

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Monomeric and dimeric Schiff bases with cyanate terminals were prepared and characterized. Polarized optical microscopy revealed the narrow mesomorphic ranges for the corresponding monomer and dimers. Cyclotrimerization of cyanate groups was identified by differential scanning calorimetry (cure exotherms between 160 and 270°C) and infra-red spectroscopy (triazine absorptions at 1567 and 1370 cm^{-1}). The cured dimers are hard and transparent.

(Keywords: Schiff base; cyanate; cyclotrimerization; liquid crystal; cure)

The inherent drawbacks of thermotropic liquid crystalline polymers, such as the maintenance of high temperature stability without reducing the ease of processability and the resulting anisotropic mechanical properties during shear flow, have stimulated research on the polymerization of low molecular weight di- or multiple-functional mesogens. Several approaches have been reported[1–3]; among them, aromatic dicyanates have interesting features with regard to the cyclotrimerization of cyanate groups and the special properties (thermal stability, toughness, low moisture absorption and low dielectric constant) of the resulting polycyanurate networks[4,5]. In this communication, the preparation of liquid crystalline Schiff bases with cyanate terminals is described and their cure behaviour reported.

Procedures for the synthesis of monomer *I*, and dimers *II* and *III* are given in *Scheme 1*. The cyanated Schiff bases were prepared from the corresponding phenols and cyanogen bromide according to the method of Grigat and Putter[6]. Crude products were purified by washing out the starting phenols with acetone and consecutive precipitations with distilled water. Selected thermograms from differential scanning calorimetry (d.s.c.) are shown in *Figure 1*. The first broad endotherm corresponds to the superimposed melting and clearing temperatures of the respective liquid crystals. The following curing exotherms appear in the temperature range of 160–270°C. The cure enthalpy for monomer *I* (90.0 kJ mol^{-1}) is higher than for dimers *II* and *III* (83.5 and 77.7 kJ mol^{-1} of OCN, respectively). The accompanying decomposition around 270°C causes upturn of the baseline and therefore a lower cure enthalpy for dimer *III*. Certain crosslinking reactions may occur during melting of dimer *II*, as evidenced by polarized optical microscopy. This concomitant crosslinking inhibited the regeneration of solid crystals of dimer *II* after cooling from 150°C to room temperature. No mesophase was detected on the heating cycle of dimer *II*. Instead, the quenched sample

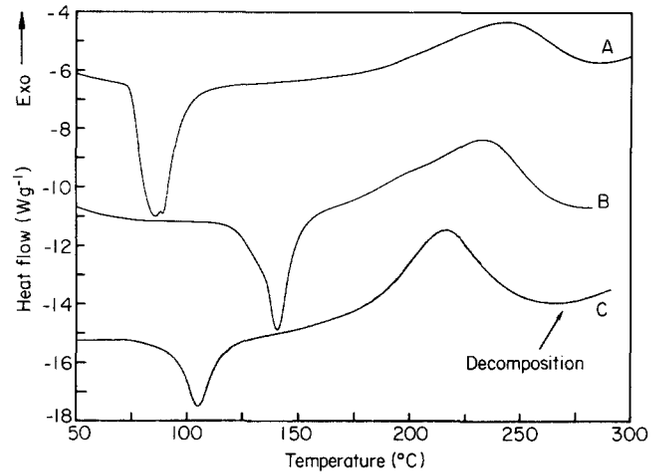

Figure 1 D.s.c. thermograms (30°C min^{-1}) for selected cyanated Schiff bases of: A, monomer *I*; B, dimer *II*; C, dimer *III*

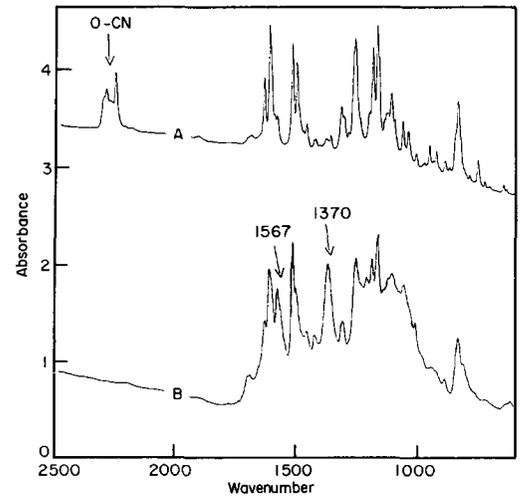

Figure 2 Infra-red spectra of: A, dimer *III*; B, dimer *III* after heating at 170°C for 5 min

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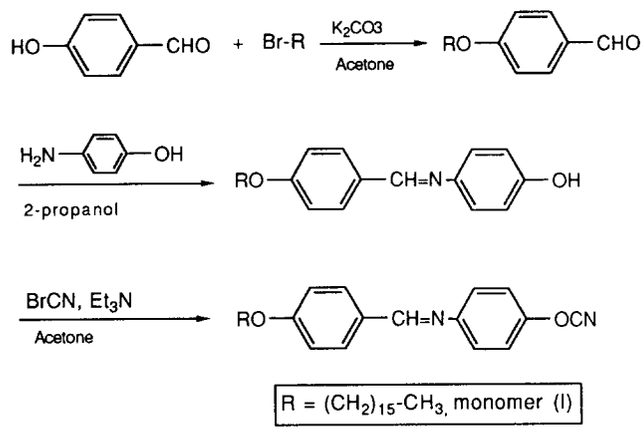
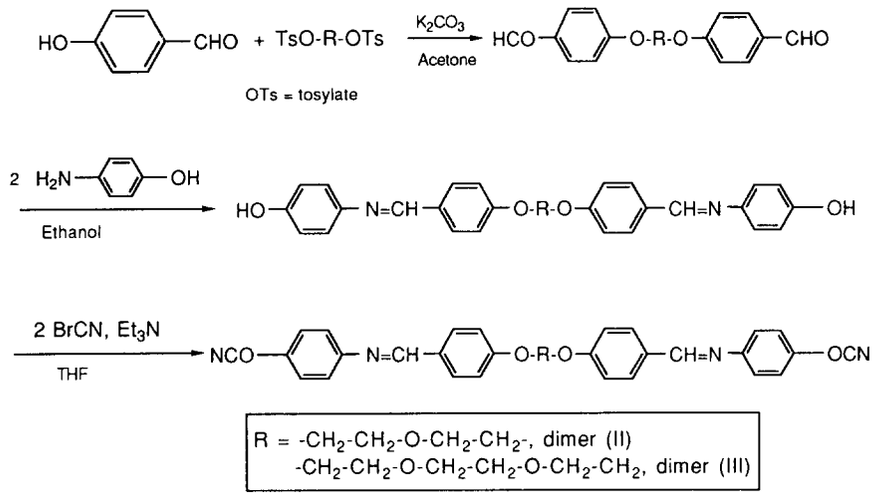
A. *Synthesis of monomer:*



B. *Synthesis of dimer*



Scheme 1 Syntheses of cyanated Schiff bases

exhibited 'frozen' mesomorphic textures under polarized light. The reversible appearance of solid crystals and mesophases for monomer *I* (87–95°C) and dimer *III* (93–123°C) under consecutive heating and cooling cycles at temperatures below cure suggests that no crosslinking occurred during melting of compounds *I* and *III*. The relatively narrow range of mesophase is attributed to the non-linear geometry of the cyanate group with respect to the neighbouring *N*-phenyl ring[7].

Cyclotrimerization was further surveyed by infra-red spectroscopy. The cyanate absorptions at 2236 and 2270 cm^{-1} completely disappear after heating dimer *III* at 170°C for 5 min (*Figure 2*). Instead, the cured dimer *III* shows the characteristic triazine absorptions at 1567 and 1370 cm^{-1}. For dimer *II*, the substantial reduction of cyanate absorptions after heating at 142°C for 3 h suggests that a certain degree of crosslinking occurred during melting. The cured products of dimers *II* and *III* are hard and transparent.

Further study can be conducted with both monomer *I* and dimers. Cyclotrimerization of monomer *I* may also yield liquid crystalline materials in view of the reported discotic 2,4,6-tris[4-(4-aminophenyl)-alkoxy]-benzylidene]-1,3-5-triazine[8]. With the dimeric system, it is interesting to study the cure kinetics and to evaluate the influence of the spacer length on the apparent activation energy and/or critical gel point. Other topics, such as the effect of catalysts on cure kinetics and polymerization under magnetic field to generate non-linear optical materials, constitute promising areas for future research.

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