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Liquid Crystalline Organisation and Reaction Rate in the Formation of Liquid Crystal Thermoset Networks from Diepoxides and Dicyanates

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Summary: The influence of the type of mesophase on the rate of reaction in amine curing or anionic polymerisation of mesogenic diepoxides, and in the cyclotrimerisation of mesogenic dicyanates has been investigated by isothermal DSC and IR-spectroscopy. Epoxide/amine systems were found to react faster in the nematic than in the isotropic phase. Anionic polymerisation of epoxides is an example where increase of the reaction rate occurs with the transition from a mesophase of higher order (smectic) to phases with lower order (nematic, isotropic). For triaromatic dicyanates with one or three methyl groups at the central ring cyclotrimerisation is faster in the isotropic than in the nematic phase showing an increase of activation energy in the nematic phase with the number of methyl groups. A pronounced rate increase has been observed in the smectic phase as compared to the nematic phase for the unsubstituted triaromatic dicyanate. In this case activation energies in the two phases are comparable with those of non liquid crystalline dicyanates.

Keywords: cyanates; epoxides; influence of mesophase; kinetics; liquid crystalline thermosets

Introduction

Densely crosslinked networks with liquid crystal like organisation of building blocks, also named liquid crystal thermosets (LCT), have attracted scientific and commercial interest during the past years. A variety of monomers with different functional groups have been reported, in particular acrylates, epoxides and cyanates.[1–3]

Reaction rates and activation energies are affected by the state of order of the medium used.[4] An effect of the mesophase type on the reaction rate during formation of LCT has been reported by several groups. Broer et al. found a rate increase in the photo polymerisation of mesogenic diacrylates.[5] In the field of step polymerisation amine curing of a mesogenic diepoxide has been reported to proceed faster after transition from an isotropic to a nematic phase.[6] Douglas et al. studied mesogenic diacetylenes by Raman spectroscopy and reported a higher reaction rate in the nematic than in the isotropic phase. As their results were obtained with two different monomers stereo-electronic effects can also be the origin of the different rates.[7] Ober et al. reported rate enhancement during cyclotrimerisation of a triaromatic dicyanate after the isotropic/nematic transition on the basis of the shape of DSC-curves without an analysis in terms of rate constants or activation energy.[8]

Unambiguous proof of a change of reaction rate caused by a phase transition requires experiments under identical conditions, one single network forming reaction, and equal reactivity of functional groups. Ideally a phase transition should take place during polymerisation which is the easiest and most reliable way to ensure identical conditions and attribute changes in the reaction rate to a change of the (meso)phase.

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Possible sequences of conservation, formation, transformation and disappearance of mesophases during conversion of a monomer to a crosslinked polymer are:

1. LC – monomer mesophase(s) LC – thermoset
2. LC – monomer mesophase(s) isotr. thermoset
3. isotr. monomer mesophase(s) LC – thermoset

In sequences 2 and 3 order decreases or increases with conversion, hence, in such systems the reaction rate in at least two different (meso)phases can be studied in one experiment, if the phase transition occurs prior to vitrification in the temperature range studied.

In this paper we present and critically discuss results obtained in our laboratory or reported in the literature in which the degree of order of a (meso)phase is claimed to be responsible for changes in the rate of polymerisation of epoxides and cyanates.

Experimental Part

Synthesis of monomers and formation of LCT has been described in previous papers: diaromatic diepoxides in references [9,10] triaromatic azomethine diepoxides in references[11,12] mesogenic triaromatic dicyanates in reference.[13] Methods of characterisation were those described in the corresponding papers.

Transformation of thermal data from DSC into kinetic data was made based on the equations given below with

p: conversion of reactive groups at a given time;
ΔH_t: reaction enthalpy for this time;
ΔH_∞: theoretical enthalpy of reaction of one mol of functional groups;
ΔH_{res}: residual heat of reaction at a given time.

$$\Delta H_\infty = \int_0^\infty \left(\frac{dH}{dt}\right) dt \tag{1}$$

$$\Delta H_t = \int_0^t \left(\frac{dH}{dt}\right) dt \tag{2}$$

$$p = \frac{\Delta H_t}{\Delta H_\infty} \cdot 100\% = \frac{\Delta H_t - \Delta H_{res}}{\mathrm{f}\, \Delta H_\infty} \cdot 100\% \tag{3}$$

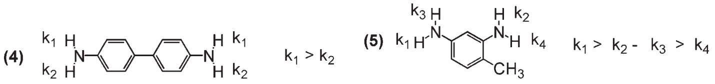
Results and Discussion

Isothermal DSC measures changes of heat flux with time. Transformation of DSC data into kinetics is made using equations 1–3. ΔH_∞ for one mol of cyanate groups was found to be -115 kJ/mol OCN for ΔH_∞. [14] Depending on reaction temperature, purity of the monomer, and type of catalyst an induction period is observed followed by a first order reaction of functional groups until vitrification occurs. [12,14]

To have additional reliable information about the reactions occuring in the DSC experiment, where heat flow can be caused by many different reactions and transitions, IR-spectroscopy was also used. The oxirane band at 918 cm^{-1} is too weak to allow for quantitative kinetic analysis. It must be mentioned that rate changes due to changes of the mesophase cannot detected in IR-spectra under any conditions. Cyclotrimerisation of dicyanate **7** did not show rate increase in the IR-studies, if the layer of monomers between the NaCl plates was too thin. We attribute this to the fact that surface effects are more important in the IR-experiments in terms of catalytic impurities as well as in terms of their influence on the formation of mesophases and their transitions. In the DSC pan the samples form a drop in one part of the pan thus reducing surface effects. Therefore, most of the kinetic results in this paper were obtained from isothermal DSC experiments.

Diepoxides

Epoxides, though of great industrial importance, are far from being suited as model compounds for kinetic studies. Amine-curing with diamines is a step reaction with a complex sequence of up to 4 different reaction rates for the individual addition steps depending on the structure of the diamine used as shown in Scheme 1.[15] It is



Scheme 1.
Rate constants for addition of epoxides to aromatic amines.

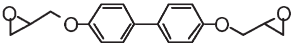
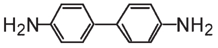
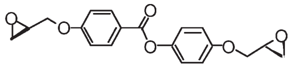
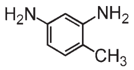
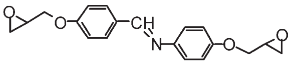
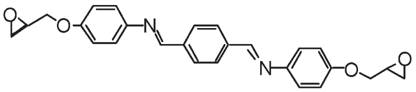
further complicated by autocatalysis from hydroxy groups formed in the addition step.[16] This makes a kinetic analysis by integral methods like DSC almost impossible. Therefore no attempt is made beyond determination of conversion at which phase transitions occur in this case. Structures and thermal properties of diepoxides and diamines used in this study are included in Table 1.

Mixtures of diaromatic diepoxides and diamines in the stoichiometric ratio of 2: 1 are isotropic, the clearing point increases as the reaction proceeds and a nematic phase appears after a certain conversion at a given temperature. [9,10] Anionic polymerisation of diepoxides on the other hand decreases the isotropisation temperature or more generally speaking the thermal stability of the mesophases.[12]

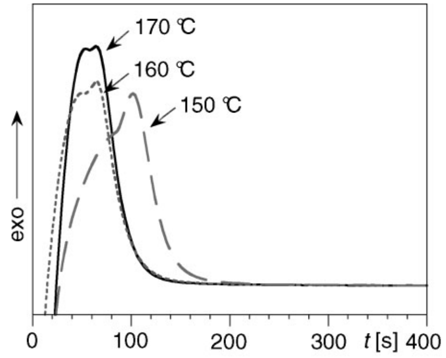
Isothermal curing of mesogenic diepoxides with diamines was made as previously described by dissolution of appropriate amounts of a diepoxide and a diamine in 1,4-dioxane and freeze-drying for intimate mixing.[10] DSC-traces for isothermal curing of 4,4′-bis(2,3-epoxypropoxy) biphenyl **(1)** with 2,4-diaminotoluene **(5)** and of 4-(2,3-epoxypropoxy)phenyl-4-(2,3-epoxypropoxy)-benzoate **(2)** with 4,4′-diaminobiphenyl **(4)** are given in Figures 1 and 2. The curves of both systems are very similar. They show two maxima, i.e., an additional increase in heat evolution after a certain time. Some results of the isothermal curing of both systems are summarized in Table 2. For **2/5** LCT were obtained up to 180 °C curing temperature. The time after which reaction rate increases corresponds well to the isotropic-nematic transition of the melt detected with polarized light microscopy. Conversion at the isotropic-nematic transitions increases from 8% at 120 °C to 14% at 130 and 19% at 140 °C. (4-(2,3-epoxypropoxy)-benzylidene-4-(2,3-epoxypropoxy)-aniline **(3)** gives similar results when cured with diamine **5**.

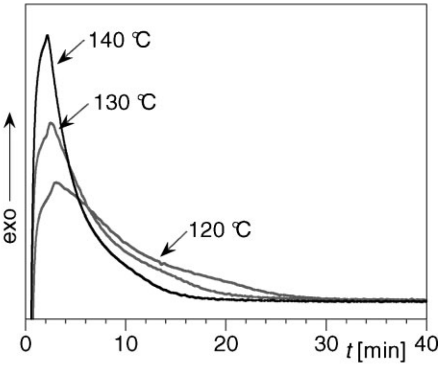
A sample of **1/5** between glass slides becomes immobile after phase transition and cannot be molten again to observe a

Table 1.
Structure and thermal properties of diaromatic diepoxides and diamines **1–6**.

no.	Structural formula (Thermal properties)	no.	Structural formula (Thermal properties)
1	 T_m 159 (n T_i^* 109 °C)	**4**	 T_m 127 (n T_i^* 17 °C)
2	 T_m 119 (n T_i 92 °C)	**5**	 T_m 99 (n T_i^* ≈ - 155 °C)
3	 T_m 130 (n T_i 128 °C)	**6**	 T_m 203 s 233 n 259 °C i)

*obtained from extrapolation.





DSC of isothermal curing 2:1 epoxide/amine mixtures

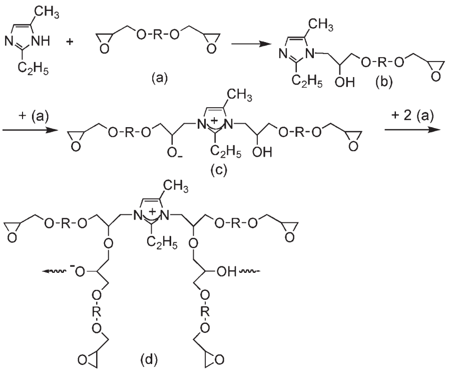
Figure 1.
Epoxide **1** and 2,4-diaminotoluene **5**.

Figure 2.
Epoxide **2** and 4,4′-diaminobiphenyl **4**.

clearing transition. X-ray studies of a solidified sample of **1/5** show sharp reflections characteristic of crystalline structures.[17] Hence in contrast to reports in the literature[6] no liquid crystalline phase is formed on curing of **1/5**, the second exotherm is caused by the heat of crystallisation.

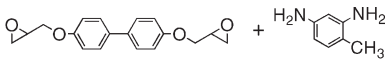
Taking into account all examples reported in the literature where an LC phase has been proven, rate enhancement in general takes place when a nematic phase is formed from an initially isotropic melt.

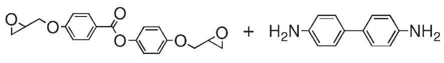
Anionic polymerisation of epoxides too is not a simple reaction though it can be described by first order kinetics with respect to the epoxy groups. Anionic polymerisation of epoxides with 2-ethyl-4-methylimidazol (EMI) has been studied by Heise and Martin.[16] The secondary amino group of EMI adds to an oxirane ring to form a tertiary amine (Scheme 2). Further reaction of the N-substituted imidazol with an epoxy group yields a zwitterionic structure with the imidazolium cation and an alkoxy anion. This starts a kinetic chain



Scheme 2.
Anionic polymerisation of diepoxides.

Table 2.
Properties of networks from diepoxide **1**, 2,4-diaminotoluene **5** (left) and diepoxide **2**, 4,4′-diaminobiphenyl **4** (right).





Tcure [°C]	$p_i \rightarrow n$/%	ΔH kJ/mol △	Phase	T_{cure} [°C]	$p_i \rightarrow y$/%	ΔH kJ/mol △	Phase
150	42	84	i → cryst.	120	8	83	i → n LCT
160	41	80	i → cryst.	130	14	83	i → n LCT
170	42	79	i → cryst.	140	19	83	i → n LCT
200		66	i → cryst.				

Table 3.
Conditions and kinetic data from polymerisation of **3**.

Meso-phase	T_{cure} 220	225	230	240	Eact. kJ/mol
	k $^*10^4$ (Δp /%)	k $^*10^4$ (Δp /%)	k $^*10^4$ (Δp /%)	k $^*10^4$ (Δp /%)	
s	2.46 (0-6)	3.53 (0-3)	4.76 (0-1)	–	134
n	4.46 (7-28)	5.01 (4-21)	6.24 (2-21)	8.76 (0-17)	73
i	7.84 (29-44)	6.73 (22-42)	11.5 (22-41)	17.3 (18-42)	86

causing branching and cross-linking when diepoxides are used as monomers.

1,4-Bis-[4-(2,3-epoxypropoxy)-phenylamino]-dibenzylidene **6** has a melting point of 203 °C, a smectic/nematic transition at 233 °C and a clearing point of 259 °C. The isothermal DSC traces in Figure 3 clearly show two or three regions depending on the curing temperature. Microscopic investigation of samples at the same temperature allows to assign the rate increase to mesophase transitions. The first increase (curves at 220, 225, and 230 °C) is due to a smectic/nematic transition, which hardly can be distinguished at 230 °C. It is absent at 240 °C, because curing starts in the nematic phase above 233 °C. The second increase is caused by the transition from the nematic to an isotropic melt.

Anionic polymerisation of **6** destabilizes the smectic phase, hence at one point the nematic phase is the most stable, while at even higher conversion there is only the isotropic phase. Thus polymerisation has the same effect as heating of a non-reacting system.

For kinetic analysis data of time intervals corresponding to a given phase separately were treated according to first order kinetics.[12] Relevant data used for calculation, ranges of conversion and the first order constants are given in Table 3. They qualitatively show that the phase transitions occur at lower conversion ($6 \rightarrow 1$ for the s/n and $28 \rightarrow 17$ for the n/i transition) if temperature is increased from 220 to 240 °C.

Arrhenius plots of the rate constants from first order treatment shown in Figure 4 give activation energies of 134, 73, and 86 kJ/mol in the smectic, nematic and in the isotropic phase respectively. Activation energies are comparable for the nematic and isotropic phase which reflects the relatively low order in nematic phase. Activation energy in the smectic phase is almost double that of the isotropic phase which is in agreement with the higher order of the smectic phase. It also implies that the parallel layer-like arrangement of monomers is far from the geometry molecules must adopt in the transition state.

The example reported here to our knowledge is the first, where a polymerisation proceeds faster in the phase with lower order.[12] Similar results have been found with ester group containing triaromatic

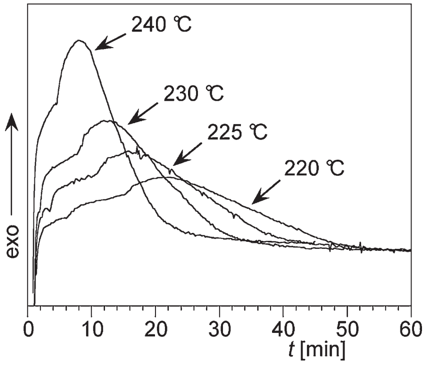


Figure 3.
DSC traces of diepoxide **6** (anionic polymerisation).

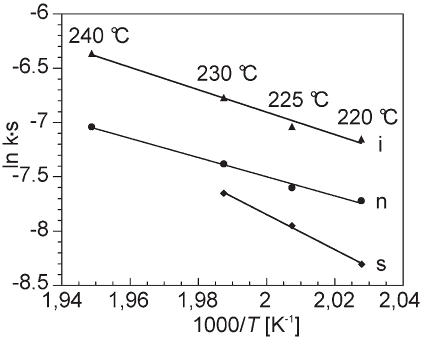


Figure 4.
Activation energies for polymerisation of **6** for different phases.

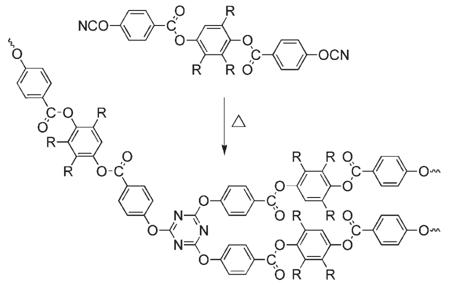
diepoxides, hence the reported behaviour seems to be a general characteristic of the anionic polymerisation of LC diepoxides.

Dicyanates

The simple and well-studied kinetics of cyclotrimerisation make cyanates preferred candidates to investigate the influence of phase transitions on the reaction rate.[19,20] In addition, integral methods like DSC can be used for kinetic analysis and results can be compared to direct measurement of concentration of functional groups, e.g., from IR-spectroscopy.[14] Dicyanates used in this study were hydroquinone-di-4-cyanatobenzoate (**7**), methylhydroquinone-di-4-cyanatobenzoate (**8**) and trimethyl–hydroquinone-di-4-cyanatobenzoate (**9**).[13] Structures and mesogenic properties of the triaromatic dicyanates **7** - **9** are given in Table 5. All have functional groups of equal reactivity which facilitates investigation of the influence of mesophase order on the rate of cyclotrimerisation. The cyanurate crosslinks formed during cyclotrimerisation are shown in Scheme 3.

Monomers **7** - **9** were cured without additional catalyst. Monitoring cyclotrimerisation by IR-spectroscopy gave time conversion diagrams shown for **7** and **8** in Figure 3. Again a rate increase is observed for **1**, while a monotonous curve is found for **2**.

Figure 6 shows a series of isothermal DSC scans of the cyclotrimerisation of dicyanate **1** at different temperatures. Each curve has two distinct maxima. The minima in-between coincide with the nematic to smectic transition, thus the shape of the curves indicates a rate enhancement due to a phase transition.



Scheme 3.
Cyclotrimerisation of triaromatic dicyanates.

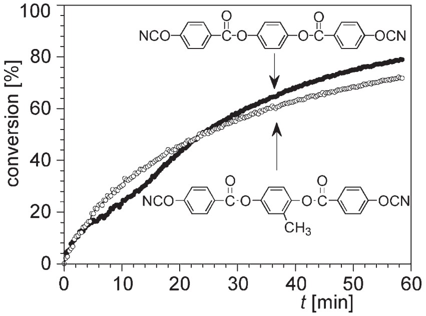


Figure 5.
Cyclotrimerisation of **7** and **8** from FT-IR-spectroscopy at 220 °C.

The nematic to smectic transition of **7** occurs between 45–65% conversion depending on the reaction temperature. First order treatment of the DSC data is shown in Figure 7. Taking into account the phase transitions and the fact that a network is formed during the reaction the curves can reasonably be divided into several ranges. The first part of the curves is the induction period in which the catalytically active species are formed (filled symbols). A first order range follows in which cyclotrimerisation takes place in the nematic phase (open symbols). The third range coincides with the nematic to smectic transition which takes place in a conversion interval in which the rate gradually increases (filled symbols). Another first order range follows (open

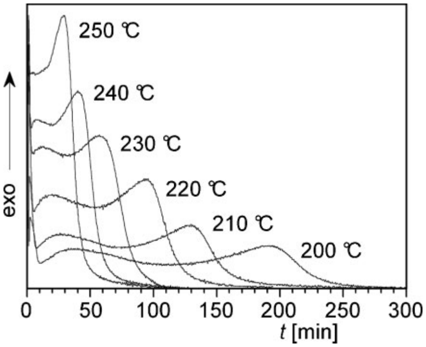


Figure 6.
Isothermal DSC traces of cyclotrimerisation of **7** at 200–250 °C.

Table 4.
First order constants of cyclotrimerisation of **1:** k_n (nematic), (k_s) smectic phase.

T [°C]	$k_n \cdot 10^4$ [s^{-1}]	$k_s \cdot 10^4$ [s^{-1}]
200	0.72	1.90
210	1.13	3.28
220	1.58	4.67
230	2.65	6.92
240	3.42	10.93
250	4.65	17.05

symbols), where the reaction proceeds in the smectic phase. The last range is characterized by a rate decrease to almost zero, which is caused by vitrification of the forming network (filled symbols).

First order rate constants are given in Table 4. They increase by a factor of almost 7 in the nematic and by a factor of nearly 10 in the smectic phase in the temperature range from 200 to 250 °C. The rate constant in the smectic phase is by a 2.5 to 4 times greater than in the nematic phase, a value beyond any doubt in terms of significance.

Activation energies in the two phases were determined from the Arrhenius equation, the plots are shown in Figure 8. Activation energies are almost identical in the nematic and in the smectic phase and well within the range of non-liquid crystalline dicyanates reported in the literature.[21] Activation energies for cyclotrimerisation of dicyanates **7** - **9** and the non-liquid crystalline 2,2-bis(4-cyanatophenyl)-propane **10** are summarized in Table 5.

The activation energies suggest that the transition state is not changed by the phase transition. The rate enhancement therefore is due to an increased pre-exponential factor which means an increased probability of functional groups to be in a favourable environment for reaction. This is schematically shown in Figure 9. The layer-like smectic organisation brings the functional groups of the mesogens closely together and in a favourable position for reaction. In the nematic phase the functional groups are distributed more along the long axis of the mesogen.

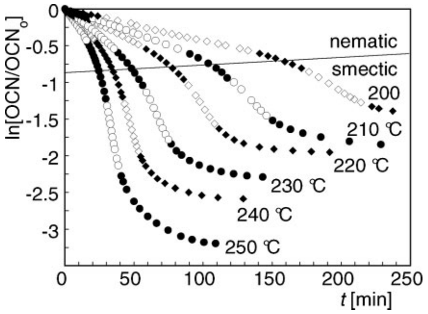


Figure 7.
First order plots of the cyclotrimerisation of **7** at 200–250 °C.

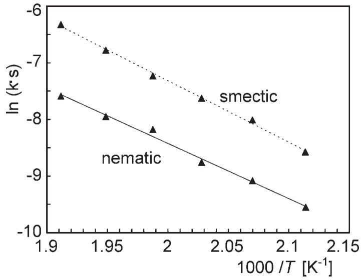


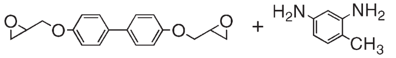
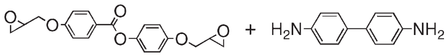
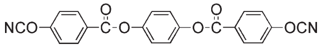
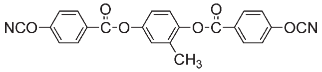
Figure 8.
Arrhenius plots of the cyclotrimerisation of **7** at 200–250 °C.

Isothermal cyclotrimerisation of **8** was studied at temperatures between 200 and 260 °C, that of **9** between 220 and 250 °C in a similar way as described for **1**. Again IR-spectroscopy proved the validity of the known mechanism and first order kinetics. **8** can be cured either in the nematic phase or initially in the isotropic and after a phase transition in the nematic phase. Dicyanate **9** can be cured only in an initially isotropic phase, which undergoes a transition to a nematic phase to give a fully cured network with nematic organisation of mesogens. A slight decrease of reaction rate has been observed for the reaction in the nematic phase as compared to the isotropic melt for monomers **8** and **9**. Cyclotrimerisation of mesogenic dicyanates seems to be the first unambiguous proof of rate enhancement after a mesophase transition observed in a step polymerisation reaction.

Conclusion

The influence of the mesophase on the rate of thermoset formation from mesogenic

Table 5.
Structure, mesogenic properties and activation energies for the cyclotrimerisation of dicyanates 2,2-bis(4-cyanatophenyl)-propane.

	10	T_m T_i [°C]	ΔH_R [kJ/molOCN]	phase	E_a [kJ/mol]
7		197 n 267	−102	n s	81.0 90.2
8		187 n 213	−108	i n	85.6 86.6
9		218 (n 163)	−116	i n	84.7 102.8
10				i	80–91.5[21]

monomers has been studied for epoxy-amine curing, epoxy polymerisation and cyclotrimerisation of dicyanates. Amine curing of mesogenic diepoxides is accompanied by an increase of the clearing temperature and of the reaction rate after an isotropic → nematic transition. Unambiguous determination of the resulting phase is a precondition to avoid errors (taking heat of crystallisation as rate enhancement).

Anionic polymerisation of a triaromatic diglycidylether resulted in a destabilisation of mesophases accompanied by a rate increase with decreasing order. Polymerisation starts in the smectic phase, which is destabilized through polymerisation, transformed into a nematic phase and finally resulting in an isotropic melt.

In the series of triaromatic mesogenic dicyanates a rate increase by a factor between 2.5 and 4 was found after a transition from the nematic to a smectic phase **(7)**. A slight decrease of reaction rate has been observed for the reaction in the nematic phase as compared to the isotropic melt for monomers **8** and **9**. Activation energies are comparable for all phases and

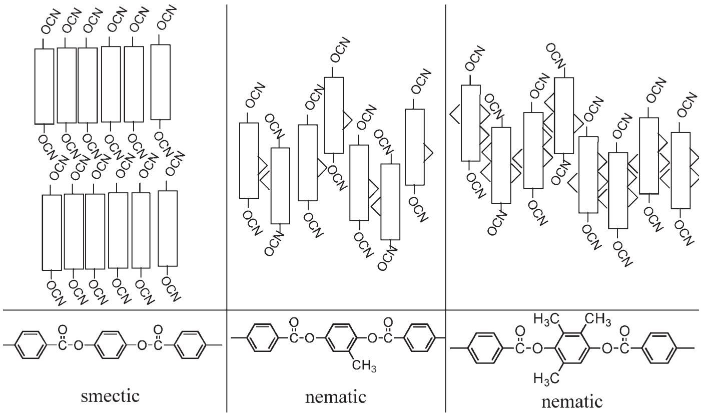


Figure 9.
Smectic and nematic organisation in the cyclotrimerisation of **7** to **9** (schematic).

are in the range reported for non-liquid crystalline dicyanates indicating that the transition state is not affected by the type of mesophase. The rate enhancement in the smectic phase can be understood in a qualitative manner, assuming that the functional groups of the dicyanates are predominantly concentrated in the boundary of the layers. The rate decrease in the nematic phase can be explained by diffusion along the long axis of the mesogens which is hindered with respect to the isotropic phase.

Obviously, the influence of a given mesophase on the reaction rate depends on the type of reaction.

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