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Liquid crystalline thermosets by polymerization of mesogenic azomethine based diepoxides-influence of reaction rate on phase behaviour

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Abstract

Five azomethine linked triaromatic (triad) mesogenic diepoxides were used to study the phase behaviour during cross-linking anionic polymerization. Clearing points and phase transitions are lowered during polymerization hence, isotropic networks are obtained from non-catalyzed isothermal polymerization. A pronounced influence of the organization of diepoxides in a mesophase on the rate of polymerization was observed for diepoxide **3** which forms a smectic and a nematic mesophase. The reaction rate increases with the smectic/nematic/isotropic transitions of the melt. Increase of the reaction rate with ethyl-methylimidazol (EMI) allows liquid crystalline phases to fix in the resulting network. Organization of anisotropic networks depends on catalyst concentration and curing temperature (reaction rate). © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Anionic polymerization; Liquid crystalline thermosets; Triaromatic mesogenic diepoxides

1. Introduction

Liquid crystal thermoset (LCT) polymers were studied by several research groups during the past decade [1,2]. Though a number of papers have appeared dealing with LCT no structure property relationships were established up to now. Although epoxy resins cannot be considered as ideal model systems [2] their great commercial importance caused us to look at this class of materials.

Networks based on mesogenic diepoxides were investigated by several groups [3–11]. Almost all papers published on epoxy LCT used amine curing as a cross-linking reaction. Several authors observed an acceleration of the curing reaction in the nematic phase. We investigated the liquid crystal properties of adducts from mesogenic monoepoxides and diamines as models for chain extended and branched intermediates (cross-link sites) formed in the amine curing of epoxides [12] and also studied amine cured epoxy resins obtained from various diaromatic diepoxides and aromatic diamines [13,14]. In a further paper we reported the synthesis and amine curing of triaromatic ester linked diglycidylethers [15].

Rozenberg [5] studied the anionic polymerization of a nematic triad diglycidyl ester. Mallon [10] and Jahromi [11] investigated the photo curing of mesogenic diepoxides with flexible spacers between the mesogenic core and the oxirane moiety. As Rozenberg studied only one monomer no structure property relations could be obtained. We synthesized a number of diad and triad diepoxides with azomethine linked aromatic rings-unsubstituted and with additional substituents in the rings which covered a wide range of melting points, liquid crystal ranges and mesophases [16]. These should enable us to learn about the influence of the structures and cross-links formed during epoxy polymerization.

The present paper deals with the results obtained from the anionic polymerization of a number of triaromatic azomethine linked diglycidylethers.

2. Results and discussion

Five different diepoxides were used in the present study. They were synthesized from suitable diamines, dialdehydes, aminophenols, and hydroxybenzaldehyde via the corresponding bisphenols, which were reacted with epichlorohydrine to yield the desired diepoxides [16]. The structures of the diepoxides are shown in Table 1.

The anionic polymerization of epoxides with EMI was studied by Heise and Martin [17]. The secondary amino group of EMI adds to an oxirane ring to form a tertiary amine (Scheme 1). A further reaction of the *N*-substituted

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imidazol with an epoxy group yields a zwitterionic structure with the imidazolium cation and an alkoxy anion. This adduct formation is considered to be the initiation process. The zwitterion is the active initiating species which starts a kinetic chain causing branching and cross-linking if diepoxides are used as monomers.

Polymerization of the diepoxides was followed by d.s.c., polarised light microscopy and in some cases by i.r.-spectroscopy. For the preparation of samples separate solutions of epoxide and catalyst in benzene or 1,4-dioxane were prepared, rapidly mixed in the desired ratio by stirring and freeze dried. The results of the isothermal polymerization are summarized in Table 1. Two sets of polymerizations were made: one with the pure monomers the other after addition of different amounts of EMI.

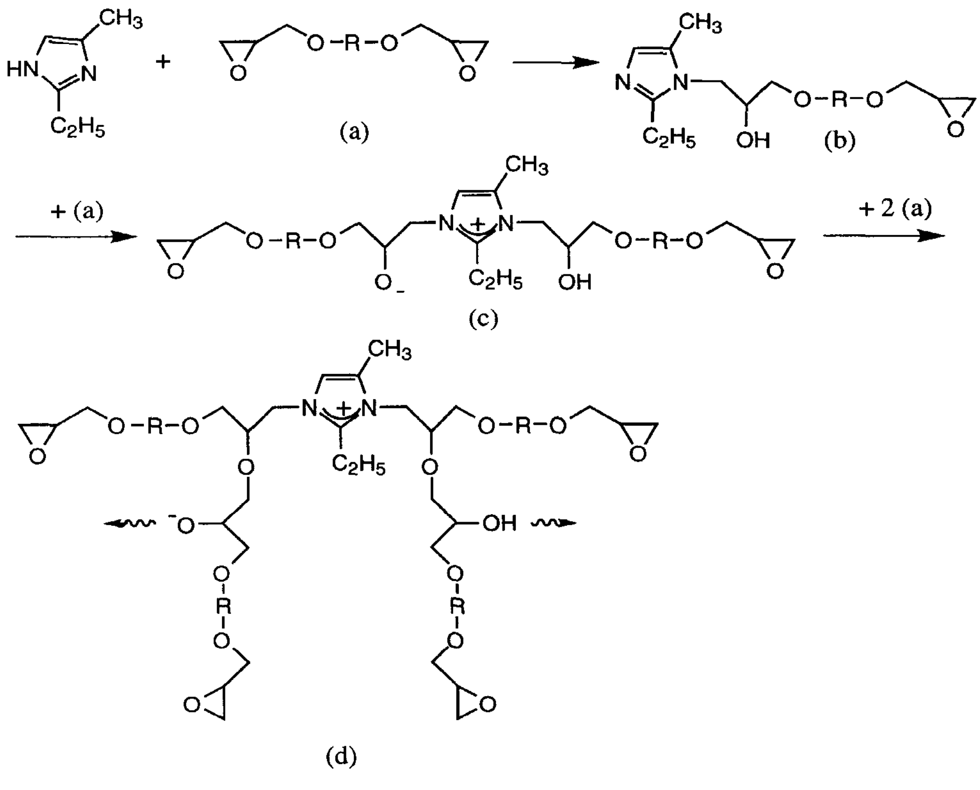
2.1. Polymerization without additional catalyst

Isothermal polymerization without catalyst was studied for all monomers except **2**. The initially liquid crystalline phases underwent a transition to an isotropic melt and no liquid crystal thermosets could be obtained. Obviously the structures formed during polymerization are unfavourable to stabilize a liquid crystalline phase. The reactions go to completion above 190°C as no additional heat is evolved in a dynamic d.s.c. scan. The glass transition temperatures of the fully cured networks are in the range of 180 to 186°C thus vitrification does not interfere with curing.

The most interesting results were observed with 1,4-bis-[4-(2,3-epoxypropoxy)-phenylamino]-dibenzylidene (**3**). Fig. 1 shows isothermal d.s.c-scans at different temperatures. **3** has a melting point of 203°C, a smectic/nematic transition at 233°C and a clearing point of 259°C. The d.s.c. traces have no monotonous curves of heat flow; they clearly show two or three regions depending on the curing temperature. These indicate that the reaction is accelerated once or twice when the thermoset is formed. Microscopic investigation of samples at the same temperature allows the assigning of rate increase to a mesophase transition. The first increase (at 220 and 225°C) is caused by a smectic/nematic transition, which cannot be distinguished at 230°C. It is absent, if curing is made at 240°C, because curing starts already in the nematic phase which is present above 233°C. The polymerization destabilizes the smectic mesophase, hence, at one point (conversion) the nematic phase is the most stable, while at still higher conversion there is only an isotropic phase. Thus polymerization has the same effect as heating of a non reacting system.

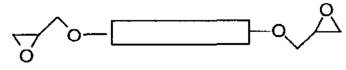
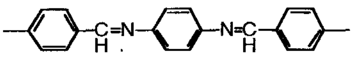
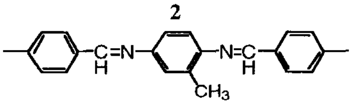
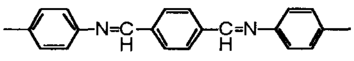
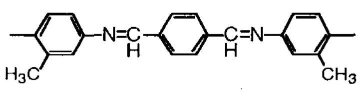
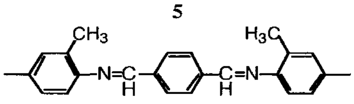
Unlike in the amine cured networks where several authors claim a rate increase, when a nematic melt is formed the anionic polymerization causes a rate increase when a transition from a higher ordered to a phase with lower order occurs.

The data from isothermal curing experiments were used for a kinetic analysis [18]. The time intervals corresponding to a given phase were treated separately according to first order kinetics. This kind of treatment is appropriate if one adopts the mechanism proposed for the anionic polymerization of oxiranes. The ranges of conversion which have not



Scheme 1.

Table 1
Structure and properties of monomers and polymers

 (Phase transitions of monomers/°C)	EMI /wt. %	Microscopy T_{cure}/°C	Microscopy Network	d.s.c. T_{cure}/°C	(ΔH / kJ/mol)
1  (k 193 n 257 i)	-	200	i	210	(75)
	0.76	200-210	i	200	(68)
	1.5	200	n	210	(78)
		210	n/i	(T_g: 180 °C)	
2  (k 130 n 228 i)	1.5	130-150	n/i	180	(69)
	8.5	130-228	n	150	(81)
				180	(70)
3  (k 203 s 233 n 259 i)	-	210-240	i	220	(71)
				230	(75)
				240	(76)
	0.26	210-230	s/n/i	210	(81)
		240	n/i		
	0.77	211-230	s	210	(74)
		240-250	s/n	240	(67)
		260	s/n/i	(T_g: 186 °C)	
		270	i		
4  (k 178 n 192 i)	-	180 - 200	i	200	(72)
	0.72	180 - 200	i	200	(68)
	1.4	180 - 200	i	200	(83)
	2.3	180 - 200	i	200	(76)
	3.5	180 - 200	i	200	(77)
	5.5	180 - 200	n/i	180	(71)
	8.3	180 - 200	n/i	180	(79)
5  (k 169 n 217 i)	-	180-200	i	200	(80)
	0.72	180-200	i	200	(77)
	1.4	180-200	n/i	200	(79)
	2.3	180-190	n/i	180	(65)
		210	i	200	(68)
	3.5	175	n	200	(81)
		180-200	n/i		
	5.7	180-200	n/s	180	(68)
	8.3	180-200	n/s	180	(65)

been considered for the kinetic evaluation are those of the initiation period and of the phase transitions. Relevant data used for calculation, ranges of conversion and the first order constants are given in Table 2. They qualitatively show that the phase transitions occur at lower conversion (6–1 for the s/n and 28–17 for the n/i transition) if the temperature is increased from 220 to 240°C.

In Fig. 2 the natural logarithm of the rate constants obtained from the kinetic analysis are plotted against the reciprocal temperature. Activation energies obtained from

Table 2
Conditions and kinetic data from polymerization of **3**

T_{cure}/°C	t_{cure}/min (conversion/%)	Type of mesophase	ln k	k
220	1.56–6.23 (0–6)	s	− 8.30	2.46×10^{-4}
	6.23–15.77 (6–28)	n	− 7.72	4.46×10^{-4}
	15.77–21.3 (28–44)	i	− 7.151	7.84×10^{-4}
225	1.36–3.33 (0–3)	s	− 7.95	3.53×10^{-4}
	3.33–10.00 (3–21)	n	− 7.60	5.01×10^{-4}
	10–15.82 (21–42)	i	− 7.037	6.73×10^{-4}
230	1.25–1.75 (0–1)	s	− 7.65	4.76×10^{-4}
	1.75–7.75 (1–21)	n	− 7.38	6.24×10^{-4}
	1.25–7.75 (0–21)	s/n	− 7.40	6.11×10^{-4}
	7.75–12 (21–41)	i	− 6.77	1.15×10^{-3}
240	0.91–4.58 (0–17)	n	− 7.04	8.76×10^{-4}
	4.58–7.88 (17–42)	i	− 6.362	1.73×10^{-3}

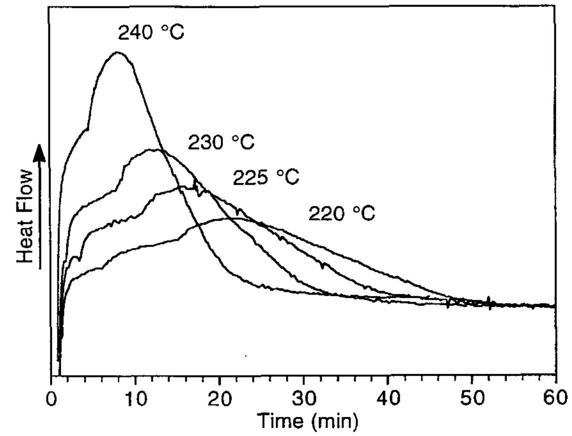


Fig. 1. Isothermal curing of **3** at different temperatures.

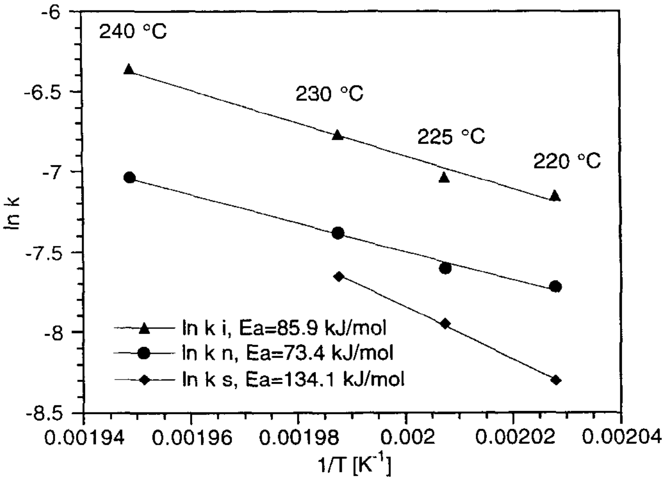


Fig. 2. Activation energies of polymerization of 3 for different phases.

these Arrhenius plots are 134, 73, and 86 kJ/mol in the smectic, nematic and in the isotropic phase respectively. The activation energies are comparable for the nematic and isotropic phase which reflects the relatively low order in nematic phase. The activation energy in the smectic phase, however is almost double that of the isotropic phase which is in agreement with the higher order of the smectic phase. This also implies that the parallel layer like arrangement of monomers is far away from the geometry the molecules must adopt in the transition state. It is also noteworthy that at 240°C the reaction should proceed faster in the smectic phase than in the nematic phase, which however cannot be proven. It cannot be explained with simple geometric arguments why the activation energy slightly increases going from the nematic to the isotropic phase. The question is whether this difference is significant at all. In order to prove the validity of the experiments we looked at the conversion time curves obtained by integration of the raw data. They are shown in Fig. 3. They have the expected shape with an initiation range followed by the polymerization. The only discrepancy arises from the 220°C curve where at a high conversion the reaction is faster than at 225°C. This, however, does not influence the kinetic treatment as far as the activation energy is concerned (Fig. 2).

The example reported here to our knowledge is the first, where a polymerization proceeds faster in the phase with a lower order.

Attempts were also made to follow the kinetics by i.r.-spectroscopy. The rather weak absorption of the oxirane ring at 914 cm^{-1} was monitored with CH vibration between 1330 and 1394 cm^{-1} as internal reference. While there is reasonable agreement in the middle range of conversion the difference in the initial and final stages is significant, favouring d.s.c. in this particular case.

2.2. Polymerization with EMI

As polymerization without EMI gave isotropic thermosets only, we studied the influence of an initiator. Samples were prepared and treated as before. The amounts of EMI used are included in Table 1 as are the temperature ranges in

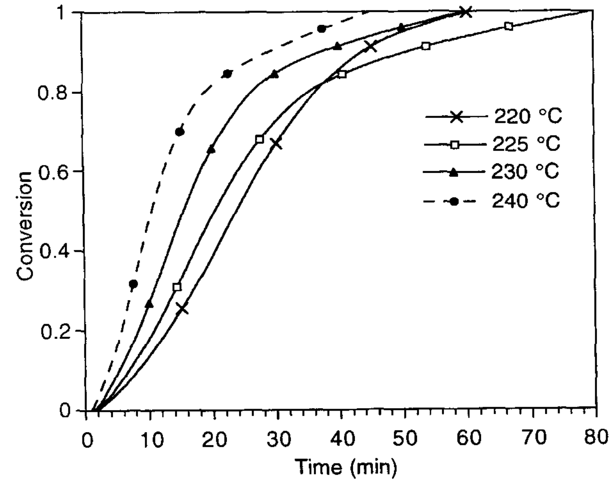


Fig. 3. Conversion time curves of polymerization of 3 at different temperatures.

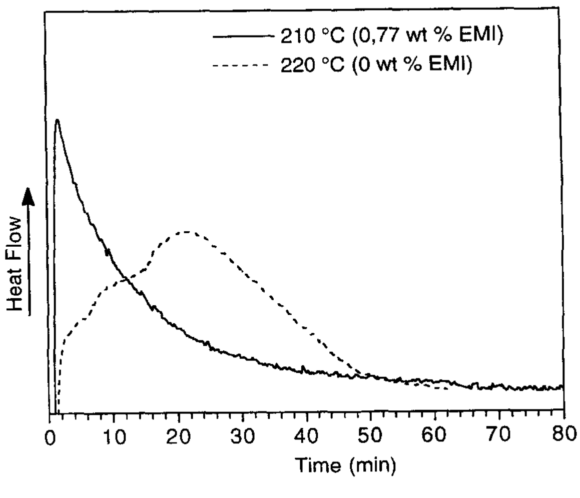


Fig. 4. Polymerization of 3 with EMI and without catalyst.

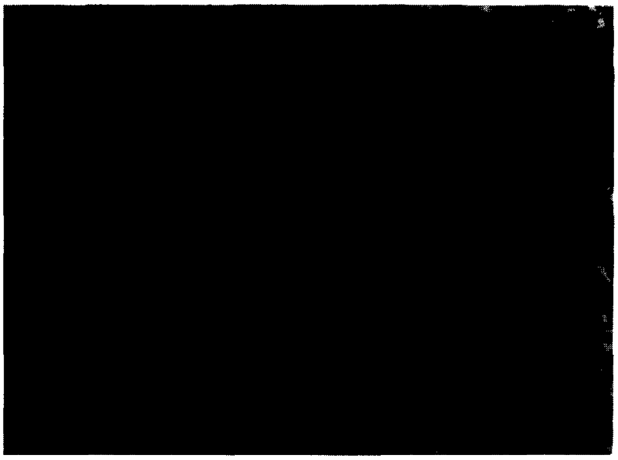


Fig. 5. Smectic phase of the LCT from **5** with 8.3% EMI polymerized at 200°C, 1 min → 150°C, 13 min → 140°C, 120 min → 200°C, 15 min.

which the isothermal reaction was studied with a given amount of initiator.

The effect of the increase of reaction rate caused by EMI is shown in Fig. 4. Polymerization of **3** in the presence of 0.77 wt% of initiator at 210°C is faster than thermal polymerization of **3** at 220°C. More important, however, is the shape of the curve. It is smooth without any additional effects like those found in the thermal polymerization. Microscopic observation of this polymerization also proves that the smectic organization is maintained in the thermoset network if the polymerization is made between 210 and 230°C. If the amount of catalyst is lowered or if the reaction temperature is increased, isotropic thermosets can be obtained at higher temperatures. By stepwise decrease of EMI or increase of temperature thermosets are accessible containing smectic and nematic regions or nematic and isotropic regions.

It is obviously possible to kinetically fix a mesophase if the cross-linking reaction is fast enough to prevent isotropization. Under appropriate conditions (temperature and catalyst) it should be possible to fix each of the mesophases the monomer shows.

The other monomers qualitatively show the same behaviour. According to their clearing points different amounts of initiator are required to obtain a liquid crystal phase. It should be pointed out that 8.5 wt% of catalyst corresponds to 27 mol%, which according to the mechanism in Scheme 1 to a large extent is amine curing rather than anionic polymerization. With this large amount of EMI LCT were obtained from all monomers, a result which is in agreement with LCT obtained from these monomers by curing with aromatic diamines [19]. It should be pointed out that with all concentrations of EMI used in these reactions cross-linked networks are formed.

Unexpected behaviour was found in the curing of **5**. At low reaction rates isotropic networks are formed, while with 3.5% EMI a nematic LCT is obtained. Further increase of EMI gives LCT with nematic and smectic regions. A nice smectic network is obtained if the mixture is polymerized in a temperature cycle (melting at 200°C, 1 min → 150°C, 13 min → 140°C, 120 min → 200°C, 15 min). Fig. 5 shows the texture obtained under these conditions.

3. Conclusions

The anionic polymerization of azomethine linked triaromatic liquid crystalline diepoxides was shown to be a suitable way to obtain liquid crystal thermosets. Under thermodynamic control no LCT can be obtained. The structures formed during polymerization destabilize a liquid crystal phase already present and prevent formation of a liquid crystal phase from an initially isotropic melt. If the rate of reaction is increased by addition of increasing amounts of EMI as initiator it is possible to trap a mesophase (kinetic control). This requires the right choice of initiator and temperature. Thus it is possible to obtain thermosets with isotropic, nematic or smectic organization of mesogens from one monomer.

The organization in a mesophase and its order were shown to have an influence on the reaction rate. A rate increase occurs going from a higher ordered to a lower ordered phase ($V_{ps} < V_{pn} < V_{pi}$).

4. Experimental

4.1. Methods of characterization

Infrared spectra were recorded on a Bruker IFS48-FT i.r. spectrometer as films between NaCl plates. A Bruker hot stage with a Eurotherm A599 processing unit was used for the high temperature measurements. Thermal transitions were investigated with a Nikon Optiphot 2 polarizing microscope equipped with a Mettler FP 82 hot stage, FP 80 processing unit and a Nikon F-601 M camera. d.s.c.-traces, transition enthalpies and temperatures were recorded with a Mettler d.s.c.30 TC 11 or TC 15-system (heating rate was 20 K/min) using nitrogen as purge gas. Investigation of the curing reaction with isothermal differential scanning calorimetry was made without waiting for temperature in the d.s.c. cell.

4.2. Materials

2-Ethyl-4-methylimidazole was a gift from the Bayer AG. Before use it was purified by destillation in a Büchi Kugelrohr apparatus. The synthesis of the diepoxides was described in a previous paper [16].

4.3. Preparation of samples for the study of the catalyzed polymerization

The diepoxide and 2-ethyl-4-methylimidazole were dissolved separately in anhydrous dioxane or benzene and mixed in the appropriate ratio (total content of solids approximately 2 wt%). These mixtures were freeze dried and the resulting powder was used for microscopy and thermal analysis.

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