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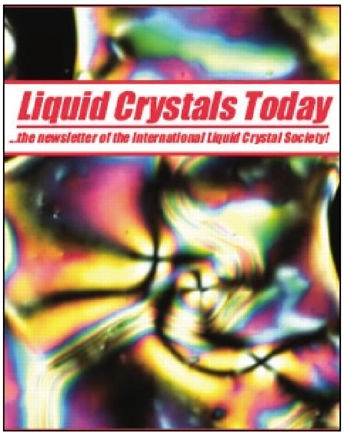

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All-aromatic liquid crystal thermosets: New high-performance materials for structural applications

T. Dingemans[a]; A. Knijnenberg[a]; M. Iqbal[a]; E. Weiser[b]; T. Stclair[b]
[a] Delft University of Technology, Faculty of Aerospace Engineering, Kluyverweg 1, 2629 HS Delft, The Netherlands [b] NASA Langley Research Center, Advanced Materials and Processing Branch, Hampton, VA, USA

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All-aromatic liquid crystal thermosets: New high-performance materials for structural applications

T. DINGEMANS*†, A. KNIJNENBERG†, M. IQBAL†, E. WEISER‡ and T. StCLAIR‡

†Delft University of Technology, Faculty of Aerospace Engineering, Kluyverweg 1, 2629 HS Delft, The Netherlands
‡NASA Langley Research Center, Advanced Materials and Processing Branch, Mail Stop 226, Hampton, VA, 23681-0001, USA

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Over the past two decades, there has been an increasing interest in all-aromatic crosslinked liquid crystal (LC) systems for structural, electronics and coatings applications. In this paper we will give a brief overview of our work on oligomeric liquid crystals end-capped with phenylethynyl reactive end-groups. All reactive oligomers were synthesized using standard melt-condensation techniques and the final products form homogeneous nematic melts over a wide temperature range (220–400 °C). The reactive LC oligomers could be cured at elevated temperatures (310–400 °C) to form true rigid-rod nematic networks. As will be demonstrated, this oligomer approach allows us to design all-aromatic nematic networks with a variety of favorable physical, mechanical and processing characteristics. Depending on the backbone chemistry, and end-group concentration, we can access liquid crystal thermosets with Tg's between 110–280 °C and storage moduli (E') of 2-5 GPa. The oligomeric nature of our reactive LCs results in excellent melt processing characteristics ($|\eta^*| \geqslant 1$ Pa.s at 100 rad.s^{-1}) and allows for the processing of complex structures such as fiber-reinforced composites. Based on our current results we are convinced that reactive all-aromatic liquid crystals can be interesting alternatives over existing high-performance polymers such as polyarylether ketones (PEEK and PEKK) polyphenylenesulfide (PPS) and polyetherimides (PEIs).

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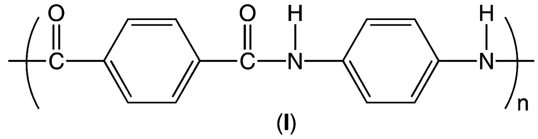
1. Introduction

Environmental and economic considerations are the main drivers behind the development of lightweight, high-strength, and high-stiffness composite materials. Traditionally, composites were considered the material of choice for the aerospace industry exclusively, but over the years composites have become enabling and affordable materials in the development of automotive applications, wind turbines and a variety of other structural applications. Current composite concepts are built around a continuous reinforcing fiber, which is imbedded in a polymer matrix. The fiber reinforcement is usually based on glass, carbon, or a liquid crystal polymer such as Zylon$^{\mathrm{TM}}$ or Twaron$^{\mathrm{TM}}$ (**I**) [1, 2].



(**I**)

The matrix resins, on the other hand, fall into roughly two categories: thermoplastics and thermosetting resins. Epoxies are well-known examples of the latter, while all-aromatic polymers such as polyphenylene sulfides (PPS), polyetheretherketones (PEEK), polyetherketoneketones (PEKK), polyetherimides (PEI) and polyethersulfones (PES) are examples of thermoplastic resins [1–4]. Epoxies have the advantage of easy processing using a variety of composite processing techniques such as Resin Transfer Molding (RTM), Resin Film Infusion (RFI), tape placement, etc. On the other hand their mechanical properties are inferior to what all-aromatic thermoplastic resins can offer. The downside of these systems, however, is that they are far more difficult to process. High processing temperatures close to the polymer decomposition temperature (>300°C) and high melt viscosities are common problems to deal with. Also, their semi-crystalline nature results in thermal stresses during cooling, which may result in micro-cracking and resin adhesion failure at the resin-fiber interface.

All-aromatic thermotropic liquid crystalline polymers (TLPCs) were considered in the past as well. Although, LCPs offer superior barrier properties, solvent resistance, ease of processing and low CTE they display low glass-transition temperatures (Tg's ~120°C) and suffer from poor adhesive properties, which has limited their use in demanding high-end applications such as composites, electronics, coatings and barrier films. Another challenge has always been to improve the melt processability of all-aromatic TLCPs. In the 1990s researchers at The

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*Corresponding author. Email: t.j.dingemans@tudelft.nl

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University of North Carolina at Chapel Hill introduced non-linear aromatic monomers, such as 2,5-substituted thiophenes, and even 1,3-substituted benzenes, without losing the liquid crystalline phase [5, 6]. They were successful in lowering the K-N transition but deviating from an ideal linear shape, however, has unfavorable consequences with respect to the phase stability, physical and mechanical properties, such as the glass-transition temperature (Tg) and the storage modulus (E′).

2. Liquid crystal thermosets

In order to improve the thermal, mechanical and processing properties, the development of thermotropic liquid crystalline thermosets (TLCTs) has attracted considerable interest. TLCTs can be regarded as networks in which the liquid crystalline organization is irreversibly fixed by a chemical reaction [7, 8]. Most work has been devoted to LC epoxy systems in the early and late 1990s. Several groups have investigated a variety of epoxy based systems, mostly built around a dihydroxy-α-methylstilbene mesogen, by Ober *et al.* [9, 10], or aromatic ester-based mesogens by Johromi *et al.* [11–14]. The general conclusion was that LC epoxies do indeed offer improved physical and mechanical properties over their non-LC epoxy-based counterparts. At the same time low-molecular-mass thermotropic monomers, end-capped with different reactive functionalities were used to prepare nematic networks. Ober *et al.* demonstrated that the cyclotrimerization of cyanate terminated mesogens results in thermally stable triazine-based nematic networks with high glass-transition temperatures (Tg ~190°C) [15]. Curing of the reactive monomers in the presence of a magnetic field resulted in well-oriented triazine networks with low values of the CTE (17 ppm/°C) in the direction of the applied field. Gavrin *et al.* functionalized their liquid crystal monomers with acetylene and phenylethynyl moieties, and observed low viscous nematic melts upon heating [16, 17]. Unfortunately, very limited mechanical and physical properties of the crosslinked thermosets were reported. The same approach was used in a series of bisacetylenes, bismaleimides, bisnadimides and bismethylnadimides, e.g. (**II**), by Benicewicz *et al.* [18–20].

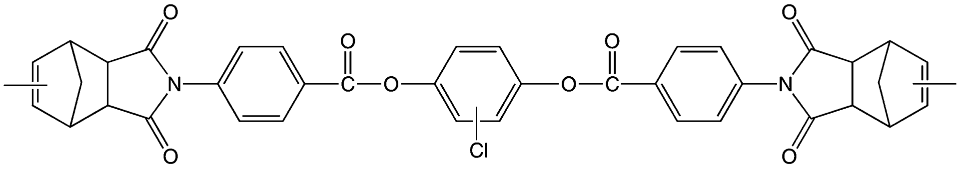
The processing window of these materials was, however, rather limited as crosslinking often started immediately after the crystal-to-nematic melt transition. In addition, starting from low-molar-mass reactive LCs, the cure kinetics and the phase behavior often appeared complex and difficult to control. Due to the high concentration of reactive end-groups, the fully crosslinked materials are characterized by their brittle nature and low fracture toughness.

3. Reactive oligomers

In order to provide TLCTs with useful mechanical, physical, and good processing properties, we have started an extensive program where we are investigating the advantages of using reactive main-chain all-aromatic liquid crystalline oligomers as precursors towards all-aromatic high modulus TLCTs with high glass-transition temperatures (Tg>200°C). This route has several advantages over using reactive low molar-mass LC monomers such as described above. We are currently exploring all-aromatic main-chain thermotropic oligomers end-capped with phenylethynyl functionalities synthesized using standard one-pot melt condensation techniques. Phenylethynyl is the only reactive functionality, so far, which survives the extreme melt condensation conditions (Tmax ~310°C) and does not crosslink or chain extend prematurely. In addition, phenylethynyl has been used extensively as a reactive end-group functionality in polyetherimides [21, 22] and the mechanical properties of the final cured products were found to be outstanding.

Another reason for using phenylethynyl is the fact that this material not only forms crosslink functionalities but can also chain-extend, depending on the concentration and temperature profile used. As investigated by Roberts *et al.* [23], phenylethynyl chain extends (e.g., via cyclobutadiene cyclodimers, and 1,5-substituted naphthalenes) and forms crosslinking functionalities (e.g., 1,3,5-trisubstituted benzenes, and polyenes). In either case, the functionalities formed do not deviate too much from linearity and hence do not disrupt liquid crystal formation.

Our initial experiments concentrated on modifying a well-known all-aromatic ester-based TLCP, Vectra™



(**II**) (K-N) 255 °C (N-I) 274 °C

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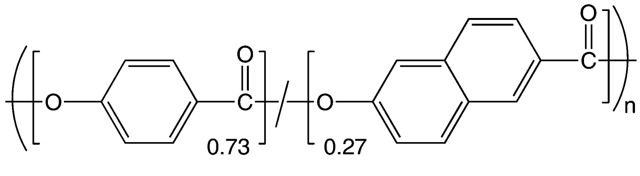
(**III**). Vectra$^{\text{TM}}$ is a random co-polymer of 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA) and this material displays a Tg of 110°C and melts into a nematic phase around 280°C [24].



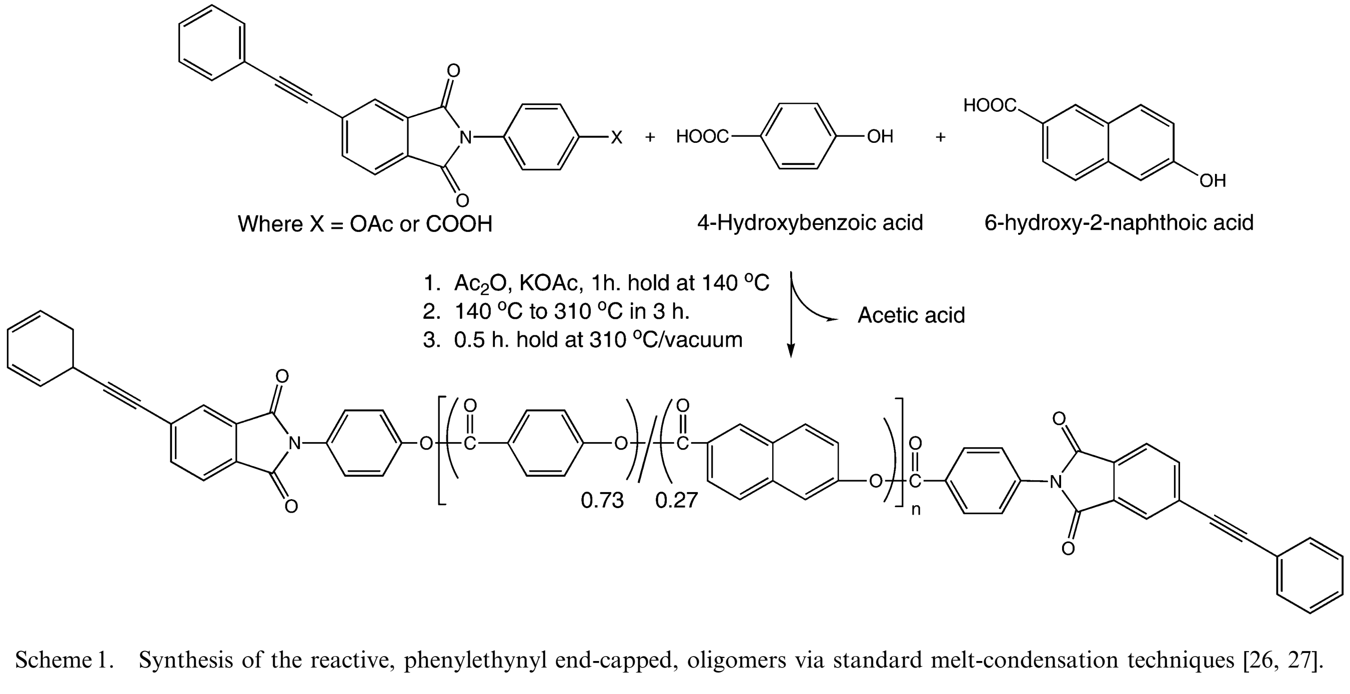
(**III**) Tg = 110 °C, (K-N) 280 °C

We prepared two series of oligomers with the aim to investigate the effects of *oligomer molecular weight* and *oligomer backbone composition* on the thermal and physical properties of reactive Vectra$^{\text{TM}}$ oligomers and their cured polymers. We used two mono-functionalized phenylethynyl end-groups, as shown in scheme 1, to effectively control the molecular weight (Mn) of the final products [25].

Using this approach we synthesized reactive oligomers with molecular weights of 1000, 5000, 9000, and 13000 g.mol^{-1} respectively [26, 27]. A high molecular weight polymer without reactive end-groups, i.e., 30000 g.mol^{-1}, was prepared as well for reference purposes. As can be expected, when increasing Mn we observed an immediate drop in the solid-to-nematic transition and the associated melt viscosity; which is advantageous with respect to processing complex structures such as fiber-reinforced composites. Figure 1 summarizes the melt and cure behavior of our reactive oligomers.

Most, if not all, commercially available all-aromatic thermotropic LCPs are random co-polymers of two or more AA/BB/AB-type monomers. All-aromatic LC homo-polymers are difficult to synthesize since they become intractable at an early stage in the polymerization. In order to obtain melt processable LCPs, a random composition is needed to suppress the melting temperature, and thus the processing temperature, to acceptable levels, i.e., <350°C. As a consequence, the glass-transition temperature (Tg) will also drop, which is not desirable since it will limit the final end-use temperature of the polymer. For example, compositions with HBA or HNA concentrations in excess of 80 mol% show a rapid increase in Tm and melt viscosity and are therefore avoided. Figure 2 shows the melting temperature (Tm) as a function of the backbone composition (HBA concentration) for the Vectra$^{\text{TM}}$ formulation without reactive end-groups.

The ability to access main-chain LCPs with, for example high HBA concentrations, is nevertheless of great interest since they will result in materials with significantly higher Tg's and E-modulus. From a commercial point of view it is desirable as well because one can formulate LCPs using cheaper backbone monomer compositions. The advantage of working with reactive oligomers is summarized in figure 2 as well. Here we show the thermal behavior of a series reactive Vectra$^{\text{TM}}$ oligomers with Mn=5000 g.mol^{-1} but with a varying HBA/HNA ratio. The melting range



Scheme 1. Synthesis of the reactive, phenylethynyl end-capped, oligomers via standard melt-condensation techniques [26, 27].

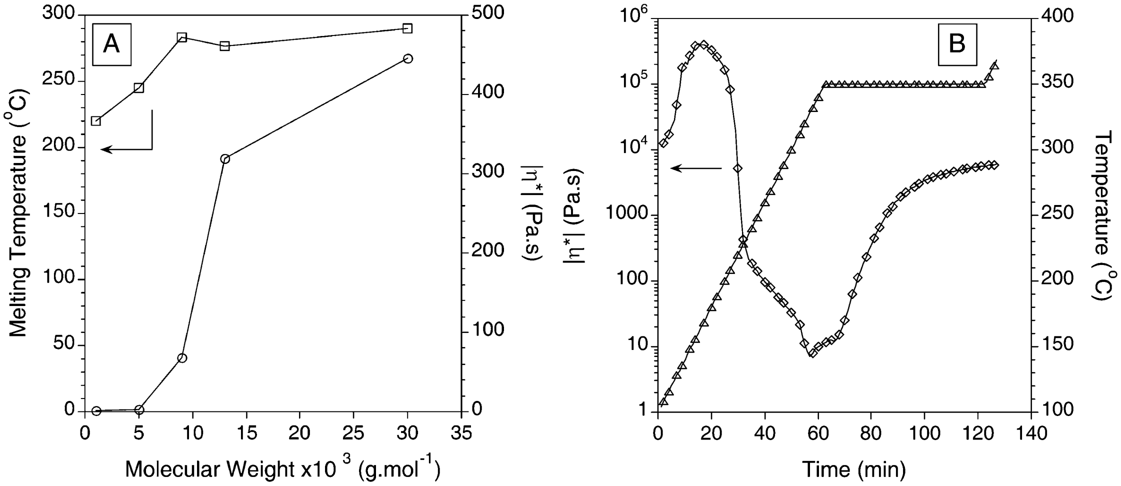


Figure 1. The melt behavior of the phenylethynyl terminated oligomers: (**A**) Tm (°C) (□) and complex melt viscosity |η*| (Pa.s) (○) as function of the molecular weight (g.mol^{-1}) and (**B**) The cure behavior of the 9000 g.mol^{-1} phenylethynyl end-capped oligomer during an isothermal hold of 1 h. at 350°C.

(Tm) becomes within acceptable limits for HBA or HNA concentrations as high as 95 mol% and these reactive oligomers could easily be processed into films. In addition, after chain extension/crosslinking the final after cure Tg is now in a range, which makes these materials interesting for a variety of high-end applications previously inaccessible. All fully cured LCTs show excellent thermal stability in both air and inert environment (N_2), and are close to 500°C (5% wt loss) [27].

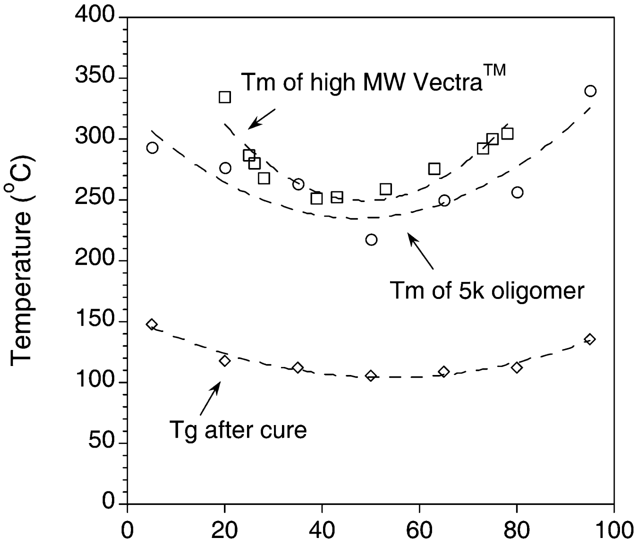
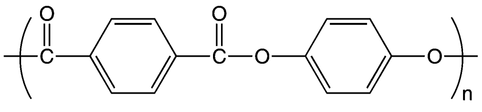


Figure 2. Melt temperature of Vectra™ as function of the [HBA] in the polymer backbone (□). Also shown is the melting temperature of a 5000 g.mol^{-1} reactive oligomer (○) and the Tg of the after cure nematic thermoset (◇).

After this proof-of-concept phase we have started to explore other more rigid ester-based backbone formulations. One of the first TLCPs investigated was based on cheap and readily available terephthalic acid (TA) and hydroquinone (HQ), or poly-(*p*-phenylene terephthalate) (**IV**).



(**IV**) Tg = 267 °C, (K-N) 610 °C (decomposition)

This LCP exhibits a Tg of 267°C, and a melting point of 610°C [28], which makes it rather intractable – the polymer in fact decomposes before it melts – and difficult to synthesize. In order to obtain a melt processable reactive oligomer, Mn has to drop to ~1000 g.mol^{-1}, which corresponds to n ~ 4. This reactive oligomer, labeled TA/HQ-1k, melts at 320°C and cures at 350°C to form a nematic thermoset with a Tg of 280°C and an E-modulus of 5 GPa at room temperature. Figure 3 shows the liquid crystalline texture before and after cure. At 350°C a low viscous nematic melt is obtained, which could easily be sheared. During the one-hour cure at 350°C the melt viscosity increases rapidly and after 45 min the nematic melt has solidified completely.

Due to the high degree of crosslinking, the films are rather stiff and show brittle fracture behavior. In order to obtain TLCTs with improved toughness, we increased the molecular weight of the TA/HQ-based oligomer precursor to 5000 g.mol^{-1}, thereby reducing the concentration of reactive end-groups, and we

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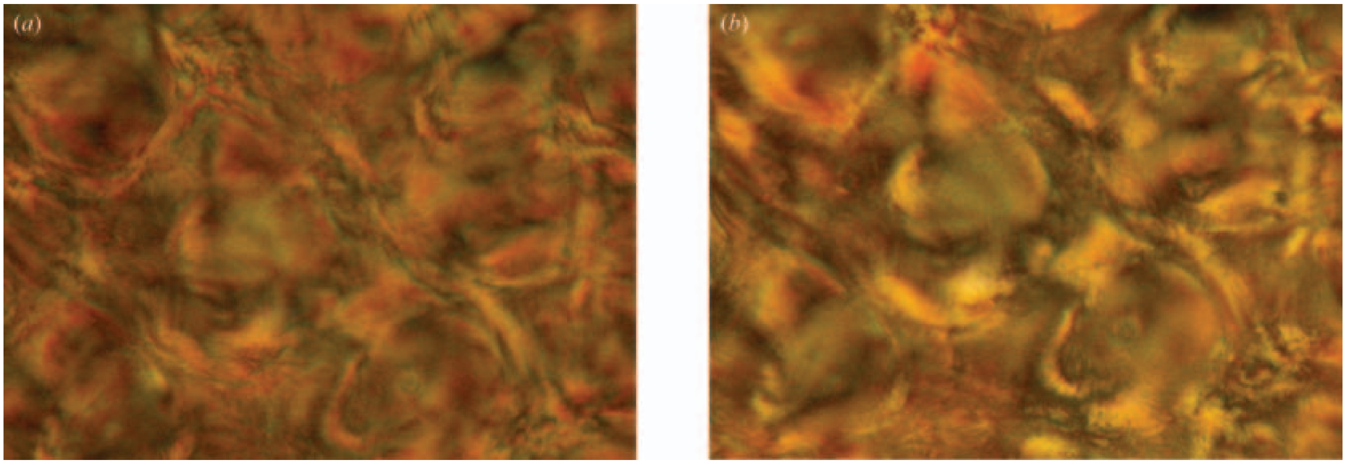

Figure 3. *A*) Nematic texture of the TA/HQ-1k melt at 350°C. ***B***) Nematic texture of the now fully cured (1 h. at 350°C) nematic thermoset; crossed polars, 50X.

modified the backbone chemistry using 50 mol% isophthalic acid (IA) or chloro hydroquinone (Cl-HQ). In both cases melt processable oligmers were obtained, which could easily be processed into fully cured thin flexible films with outstanding thermal and mechanical properties. Figure 4 shows our Dynamic Thermal Mechanical Analysis (DMTA) results of two LCT films, i.e., TA/HQ/IA(50)-5k and TA/Cl-HQ-5k.

Both film shows excellent cryogenic and high temperature behavior. TA/HQ/IA(50)-5k, figure 4a, displays a low temperature β-transition at -100°C, followed by the α-transition or Tg, as measured at the maximum of tan δ at 1 Hz, at 220°C. Once the polymer passed through the Tg, a rubber plateau is reached, which extends from 250–350°C. The storage modulus remains relatively constant at 200 MPa. Figure 4b shows the results for TA/Cl-HQ-5k, an LCT with a more rigid backbone composition. This nematic thermoset shows a β-transition and Tg significantly higher as observed for TA/HQ/IA(50)-5k, i.e., 0°C and 275°C respectively. After the experiment was terminated at 475°C, the retrieved film was still flexible, which demonstrates the unusual mechanical behavior of these materials. Other backbone variations with 6-hydroxy-2-naphthoic acid (HNA) or 4-hydroxybenzoic acid (HBA) lead to similar results and give TLCTs

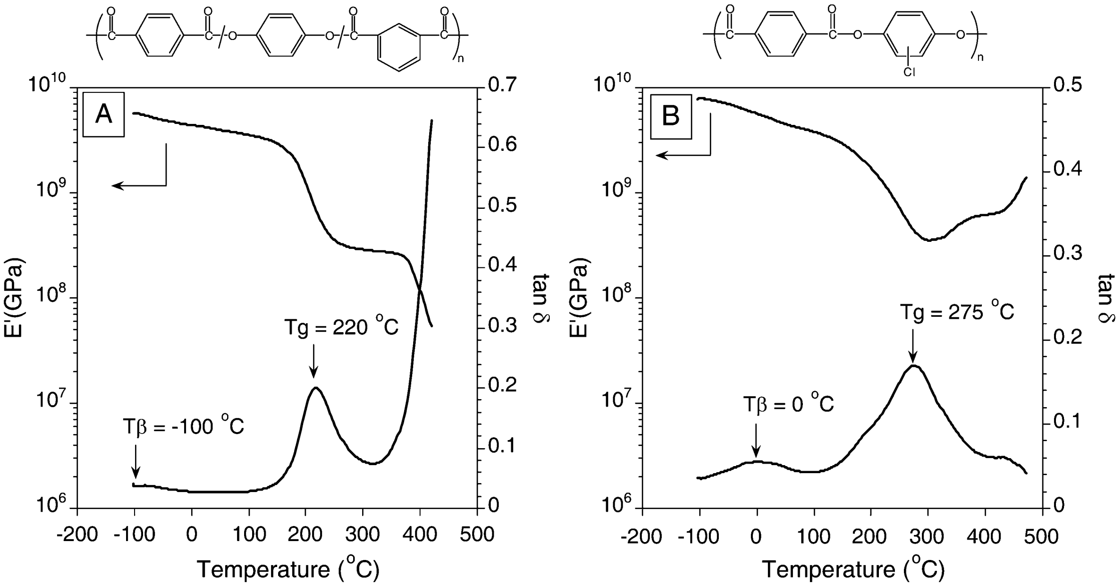

Figure 4. Storage modulus (E′) of the cured films with different chemical compositions: (**A**) TA/HQ/IA(50)-5k after 1 h. cure at 350°C and (**B**) TA/Cl-HQ-5k after 1 h. cure at 350°C. All measurements were conducted at a frequency of 1 Hz, while heating at 2°C.min^{-1}.

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Table 1. Mean shear strengths measured for a cured 9000 g.mol^{-1} Vectra-based oligomer on titanium (Ti, 6Al-4V) at room temperature [26].

Bond Pressure (kPa)	Area of overlap (inch^2)	Mean shear strength (MPa)
105	0.5	20
350	0.5	22
700	0.5	24

with outstanding physical and mechanical properties [29].

4. Concluding remarks and outlook

Herein we have given a brief overview on the different synthetic routes towards liquid crystal thermoset materials. Although LC thermosets were first considered by DeGennes in the 1970s little progress has been made with respect to understanding their underlying physics. Warner and Terentjev used the classic Theory of Rubber Elasticity as a basis to explain some of their unusual physical and mechanical properties [30]. Our main-chain reactive oligomers may offer a relatively simple set of model compounds where we can control the rigidity of the backbone and the crosslink density. Such materials could provide experimental data with respect to the entropy of such networks and the enthalpic interactions with the mesogenic backbone. Despite the fact that TLCT's remain challenging from a theoretical perspective, all-aromatic reactive LC oligomers are now commercially available and new applications in areas such as electronics, composites and coatings are emerging. Our initial work on carbon- and glass-reinforced composites indicates that their mechanical performance is superior to that of state-of-the-art epoxy based composites. This is rather promising since LCPs were shown in the past to have very poor adhesive properties to glass and carbon fiber. The adhesive properties of our reactive oligomers on carbon, aluminum, and titanium are excellent. Lap-shear strengths of 22 MPa could be measured, which are a 20-fold improvement over traditional high molecular weight LCPs, see table 1.

Based on our current results we believe that TLCTs are becoming interesting alternatives for current high-performance polymers such as, for example, PEEK and PEKK. The combination of outstanding physical, thermal, mechanical characteristics and ease of processing will make them useful for a variety of aerospace, electronic, coating and other demanding applications.

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