Synthesis and Characterization of Aryl Ethynyl Terminated Liquid Crystalline Oligomers and Their Cured Polymers

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ABSTRACT: In this paper the synthesis and characterization of two series wholly aromatic, main-chain, reactive liquid crystalline oligomers is reported. Phenylethynyl end-capped oligomers, based on 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA), were successfully synthesized using standard high-temperature melt-condensation techniques. Melt processable oligomers, with M_n = 1000, 5000, 9000, and 13 000 g mol^{-1}, and oligomers with HBA or HNA concentrations as high as 95 mol % were prepared. All oligomers showed well-defined, homogeneous, nematic melt behavior over a broad temperature range. The phenylethynyl end-capped oligomers could be cured at 370 °C and formed films with excellent mechanical and thermal properties, and without losing the nematic order. Low molecular weight oligomers, i.e. M_n < 5000 g mol^{-1}, tend to form nematic thermosets, while oligomers with M_n > 5000 g mol^{-1}, polymerize predominantly via chain extension chemistry. The fully cured nematic polymers exhibit glass-transition temperatures (T_g) up to 203 °C, as determined by DMTA measurements, and thermal stabilities (5 wt % loss) up to 500 °C in both air and nitrogen atmosphere. The cured 1000 and 5000 g mol^{-1} oligomers, with 95 mol % HBA or HNA compositions, show significant improvements in storage modulus at elevated temperatures as compared to their high-molecular weight counterparts. Rheology experiments showed that these reactive nematic oligomers are melt-stable for at least 30 min at 300 °C and exhibit complex melt viscosities $|\eta^*|$ as low as 1 Pa·s at 100 rad·s^{-1}. In all examples no loss of mesophase could be observed during chain extension or cross-linking, which indicates that phenylethynyl cross-link chemistry is completely compatible with mesophase formation.

1. Introduction

Main-chain, wholly aromatic, thermotropic liquid crystalline polymers (TLCPs) are a well-known class of high-performance polymers, which offer a unique combination of desirable properties, such as excellent solvent resistance, outstanding mechanical properties, a low coefficient of thermal expansion (CTE), and easy processing.[1−3] TLCPs have been used extensively as resins toward high-modulus fibers, coatings, and molded articles. Their use as resins for the fabrication of fiber reinforced high-performance composite articles, however, has been limited due to high melt viscosities and poor resin-fiber interfacial strength.[4] The challenge has always been to improve the melt processability of TLCPs by introducing nonlinear aromatic monomers, such as substituted naphthalenes, 2,5-thiophenes, and even 1,3-substituted benzenes, without losing the liquid crystalline phase.[5−7] Deviating from an ideal linear shape, however, has unfavorable consequences with respect to physical and mechanical properties, such as the glass-transition temperature (T_g) and the tensile modulus.

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.[8,9] Several groups have investigated a variety of reactive thermotropic systems. Low molecular mass mesogenic monomers, end-capped with different reactive functionalities were investigated by Gavrin et al.[10,11] They functionalized their liquid crystal monomers with acetylene and phenylethynyl moieties and observed low viscosity nematic melts upon heating. However, very limited mechanical and physical properties of the cross-linked thermosets were reported. The same approach was used in a series of bisacetylenes,[12] bismaleimides, bisnadimides, and bismethylnadimides by Hoyt and Benicewicz.[13,14] The processing window of these materials was, however, rather limited as cross-linking 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.

To provide TLCTs with useful mechanical properties, high glass-transition temperatures, and good processing characteristics, we report on the synthesis and characterization of a novel phenylethynyl terminated liquid crystal oligomer, build around 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA). In particular we investigated the effects of *oligomer molecular weight* and *oligomer backbone* composition on the thermal and physical properties of the reactive oligomers and their cured polymers. To the best of our knowledge, this is the first time that a liquid crystal thermosetting oligomer was prepared using a standard one-pot melt condensation technique.

2. Experimental Section[15]

Materials. All chemicals were obtained from the indicated sources and used as received. For the end group syntheses, 4-phenylethynylphthalic anhydride was purchased from Daychem. 4-Aminobenzoic acid, 4-aminophenol, and acetic acid were obtained from Aldrich. For the oligomer syntheses we obtained 4-hydroxy-

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benzoic acid (HBA) from Aldrich, 6-hydroxy-2-naphthoic acid (HNA) from Ueno Fine Chemicals LTD, acetic anhydride from J. T. Baker and potassium acetate from Acros Organics.

Characterization. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker Avance 300 MHz spectrometer (300 and 75.46 MHz). To confirm the targeted molecular weights in both series of oligomer precursors, inherent viscosities were determined using an Ubbelohde capillary viscometer. Solutions (0.5 g/dL) were prepared by dissolving the oligomer precursors in pentafluorophenol at 60 °C, followed by filtration of the solutions (pore size 0.45 μm, Teflon). Infrared spectra were collected using a Nicolet Magna-IR spectrometer 750 and thermal properties were investigated using a PerkinElmer Pyris Diamond TG/DTA, and a PerkinElmer Sapphire DSC, respectively. Unless stated other wise, samples of approximately 5 mg were investigated using a heating rate of 10 $°C\cdot min^{-1}$, using either nitrogen or air as a purge gas (20 $cm^{3}\cdot min^{-1}$). The mesophase behavior was investigated using a Leica DMLM polarizing optical microscope (POM), equipped with a hot-stage, and X-ray diffraction (XRD) analysis was conducted on a Bruker AXS D8 Discovery diffractometer, using a Cu Kα X-ray tube (λ = 1.54 Å) at 40 keV. The melt behavior of the liquid crystalline oligomers was investigated on a Rheometrics System 4 rheometer at a heating rate of 4 $°C\cdot min^{-1}$ under a nitrogen atmosphere. Sample disks (2.54 cm in diameter and 1.5 mm thick) were prepared by compression molding the oligomer powders at room temperature, and the measurements were conducted at a variable strain and a fixed angular frequency of 100 $rad\cdot s^{-1}$. Dynamic mechanical analysis was performed on a PerkinElmer Diamond DMTA, using thin films (20 mm × 5 mm × ~0.25 mm) under a nitrogen atmosphere and a heating rate of 2.5 $°C\cdot min^{-1}$. The films were prepared by melt pressing the reactive oligomers in a press for 1 h at 370 °C.

Synthesis of Phenylethynyl End Groups. A 2-L Erlenmeyer flask equipped with a mechanical stirrer and reflux condenser was charged with 1 L glacial acetic acid and 4-phenylethynylphthalic anhydride (0.5 mol, 124.12 g). The mixture was slowly heated to ~110 °C and when all solids were dissolved, 4-aminobenzoic acid (0.5 mol, 68.57 g) was added. A thick suspension formed almost immediately and was stirred for 2 h at reflux temperature. After the reaction mixture was cooled to ~70 °C, the precipitated crystals where collected by filtration and washed with acetic acid (2×) and ethanol (2×). The off-white *N*-(4-carboxyphenyl)-4-phenylethynylphthalimide (**PE-COOH**) was dried under vacuum at 150 °C for 48 h. Yield: 175 g (95%), ^{1}H NMR (DMSO-d_6, 300 MHz, 80 °C): δ 7.44−7.52 (m, 3H), 7.58−7.68 (m, 4H), 7.99−8.14 (m, 5H), 12.95−13.35 (s, COOH). ^{13}C NMR (DMSO-d_6, 75 MHz, 80 °C): δ 88, 93.5, 121.4, 123.9, 125.9, 126.9, 128.6, 128.9, 129.6, 129.9, 130, 130.7, 131.8, 132.2, 135.7, 137.3, 165.9, 166, 166.7. IR (KBr): 1716, 1775 (imide), 2250 (acetylene) cm^{-1}.

N-(4-Hydroxyphenyl)-4-phenylethynylphthalimide (**PE-OH**) was prepared in a similar fashion, however, after the initial workup the phenol end group was acetylated by refluxing PE-OH in anhydrous acetic anhydride for 2 h. *N*-(4-Acetoxyphenyl)-4-phenylethynylphthalimide (**PE-OAc**) precipitated as bright yellow crystals upon cooling. The title compound was washed with acetic acid (2×) and ethanol (2×), and dried under vacuum at 150 °C for 48 h. Yield: 184 g (96%), ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.31 (s, 3H), 7.23 (d, J = 9 Hz, 2 H), 7.35−7.42 (m, 3H), 7.42−7.5 (d, J = 35 Hz, 2 H), 7.5−7.7 (m, 2H), 7.9 (d, J = 0.01 Hz, 2 H), 8.05 (s, 1H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 21.1, 87.5, 94.1, 121.8, 122.1, 123.6, 126.4, 127.2, 128.3, 128.8, 129.1, 129.9, 130, 131.7, 131.7, 137, 149.7, 166.2, 166.2, 168.8. IR (KBr): 1695, 1772 (imide), 2220 (acetylene) cm^{-1}.

Synthesis of the Phenylethynyl End-Capped Oligomers. Both series of oligomers were synthesized using standard melt condensation techniques.[16,17] In the first series, four reactive oligomers with a target M_n of 1000, 5000, 9000, and 13 000 g mol^{-1} were prepared by controlling the concentration of reactive end groups using the Carothers equation.[18] The samples were labeled, LCR-**1k**, LCR-**5k**, LCR-**9k**, and LCR-**13k** respectively. A reference polymer, M_n ~ 30 000 g mol^{-1}, without reactive end groups, was synthesized by us as well and labeled LCR-**30k**. In the second series we varied the backbone composition of a 5000 g mol^{-1} oligomer, by varying the HBA to HNA molar ratio: 5/95, 20/80, 35/65, 50/50, 65/35, 80/20, and 95/5. These samples were labeled 05-LCR-**5k**, 20-LCR-**5k**, 35-LCR-**5k**, 50-LCR-**5k**, 65-LCR-**5k**, 80-LCR-**5k**, and 95-LCR-**5k** respectively.

Table 1. Transition Temperatures (°C) and Enthalpies (kJ mol^{-1}) of the Reactive end groups

name	T_m (°C)/ΔH_f (kJ mol^{-1}) peak	exotherm (°C) onset	peak	end	ΔH_{exo} (kJ mol^{-1})
PE-COOH	346 (*14*)	355	375	412	−21
PE-OAc	236 (*11*)	340	390	410	−33

Table 2. General Properties of the Reactive Oligomers,[a] Where the HBA Concentration = 73 mol % and the HNA Concentration = 27 mol % and the Molecular Weight Is Varied from 1000 to 13 000 g·mol^{-1}

name	target mol wt (g/mol)	yield (g)	η_{inh} (dL/g)	M_v[b] (g/mol)
LCR-**1k**	1000	276 (95%)	0.17	839
LCR-**5k**	5000	298 (98%)	0.83	4146
LCR-**9k**	9000	278 (97%)	2.05	10 438
LCR-**13k**	13 000	274 (98%)	2.99	15 292
LCR-**30k**[c]	30 000	251 (94%)	5.75	29 919

[a] A high molecular weight LCP (LCR-**30k**), without reactive end groups, was made as a reference material. [b] The M_v was calculated using the Mark−Houwink−Sakurada relationship, where $K = 2.36 \times 10^{-4}$ and $a = 0.98$.[19] For simplification, the intrinsic viscosity was assumed to be equal to the inherent viscosity. [c] Reference polymer without reactive end groups.

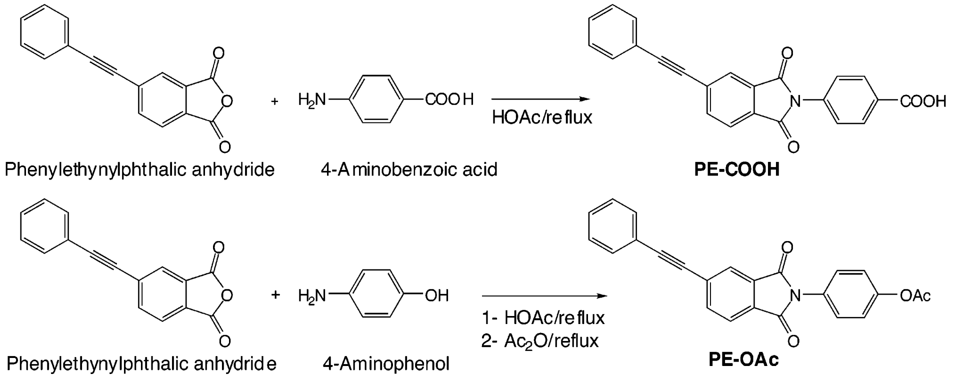
Table 3. General Properties of the Oligomers with a Target Molecular Weight of 5000 g·mol^{-1}, and Variable HBA/HNA Backbone Compositions

name	HBA (mol %)	HNA (mol %)	yield (g)	η_{inh} (dL/g)	M_v[a] (g/mol)
05-LCR-**5k**	5	95	170 (89%)		
20-LCR-**5k**	20	80	170 (93%)	0.96	4825
35-LCR-**5k**	35	65	163 (94%)	0.92	4603
50-LCR-**5k**	50	50	154 (94%)	0.83	4198
65-LCR-**5k**	65	35	141 (90%)	0.72	3589
80-LCR-**5k**	80	20	141 (96%)	0.81	4055
95-LCR-**5k**	95	5	122 (88%)	-	-

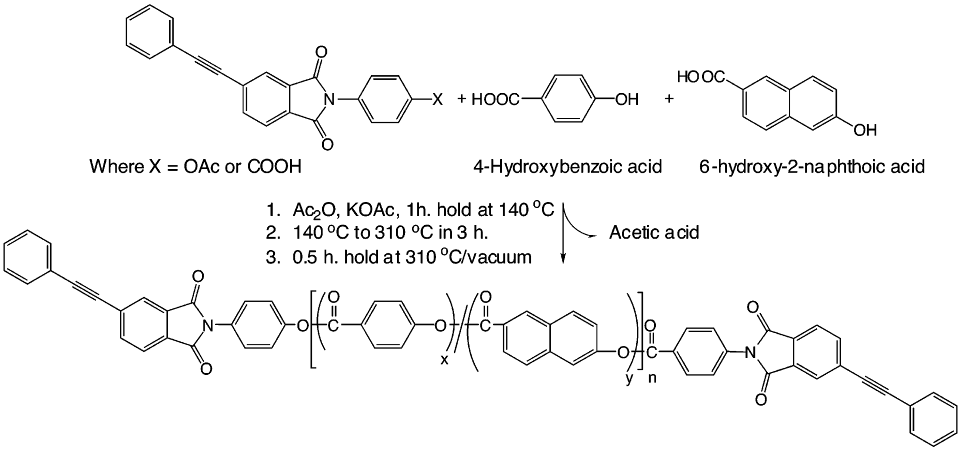
[a] The M_v was calculated using the Mark−Houwink−Sakurada relationship, where $K = 2.36 \times 10^{-4}$ and $a = 0.98$.[19] For simplification, the intrinsic viscosity was assumed to be equal to the inherent viscosity.

As a representative example we describe the synthesis of a 13 000 g mol^{-1} reactive oligomer with a 73 mol % HBA/27 mol % HNA backbone composition, i.e. LCR-**13k**: A 1000 mL three-neck round-bottom flask equipped with sealed glass paddle stirrer was flushed with nitrogen, and charged with 4-hydroxybenzoic acid (HBA) (1.46 mol, 201.6 g), 6-hydroxy-2-naphthoic acid (HNA) (0.54 mol, 101.6 g), *N*-(4-acetoxyphenyl)-4-phenylethynylphthalimide (**PE-OAc**) (0.018 mol, 6.86 g), *N*-(4-carboxyphenyl)-4-phenylethynylphthalimide (**PE-COOH**) (0.018 mol, 6.60 g) and potassium acetate (0.2 mmol, 20 mg). After adding acetic anhydride (198.15 mL, 2.10 mol), the reaction mixture was slowly stirred under a nitrogen atmosphere and heated to 140 °C to allow acetylation to take place. After a 1 h isothermal hold, the temperature of the reaction mixture was slowly increased to 330 °C using a heating rate of 1 $°C\cdot min^{-1}$. During this process acetic acid was collected as the condensation byproduct. During the final stages of the polymerization the nitrogen flow was cut off and a vacuum was applied in order to remove the last traces of acetic acid. The reaction flask was allowed to cool overnight, and the final product was removed from the flask and processed into a powder. To ensure that all acetic acid was removed we dried the powder under vacuum at 250 °C for 24 h. Yields for the syntheses were generally above 95%, and they are listed in Tables 2 and 3.

Scheme 1. Synthesis of the Phenylethynyl Reactive End Groups



Scheme 2. Melt Polymerization Route toward the Synthesis of the Liquid Crystal Oligomers with Phenylethynyl Reactive End Groups



3. Results and Discussion

Synthesis of Reactive End Groups. The reactive end groups, *N*-(4-carboxyphenyl)-4-phenylethynylphthalimide (**PE-COOH**), and *N*-(4-acetoxyphenyl)-4-phenylethynylphthalimide (**PE-OAc**) were synthesized in high yields from 4-phenylethynylphthalic anhydride, and 4-aminobenzoic acid or 4-aminophenol, respectively, using a standard acid-catalyzed imidization technique (Scheme 1).

The thermal stability of the reactive end groups is important because during the melt polymerization the oligomers will be exposed to reaction temperatures of 320−330 °C, which means that the end groups have to remain dormant to prevent premature cross-linking in the reactor vessel. To this end the thermal behavior of **PE-COOH** and **PE-OAc** was investigated using DSC, the DSC traces are shown in Figure 1.

Both compounds show sharp melting endotherms at 346 and 236 °C respectively, followed by a broad exothermic event, which starts around 340 °C and persists until 400 °C, and is due to cross-linking of the phenylethynyl end groups. The presence of the carboxylic acid and acetoxy functionalities does not seem to have an effect on the cure temperature. Both compounds, **PE-COOH** and **PE-OAc**, show cure behavior over a temperature range that does not interfere with melt polymerization conditions. The DSC results are summarized in Table 1.

Synthesis of the End-Capped Oligomers. The phenylethynyl-terminated liquid crystal oligomers were synthesized as represented in Scheme 2.

Both series of LC oligomers could be synthesized in high yields using a convenient "one-pot" step-growth melt polymerization technique. All formulations formed homogeneous nematic melts and no melt solidification, a sign of premature cross-linking, could be observed, indicating that the reactive end groups remain latent during the course of the polymerization. Even the 5000 g mol^{-1} formulations, where we used 95 mol % HBA or HNA, could be prepared without any problems. In the past, it appeared impossible to prepare such "true rigid rod" polymeric systems because the polymer melt would solidify prior to reaching high molecular weight (often $T_m \gg T_{dec}$).[3] In our case, the accessible melt temperature is a direct consequence of preparing low-molar-mass reactive oligomers.

Unfortunately, the rigid-rod and high aromatic character of our oligomers precludes size exclusion chromatograph (SEC) measurements. To verify the average molecular weight of our oligomers we performed inherent viscosity measurements in pentafluorophenol (PFP) at 60 °C. From these measurements

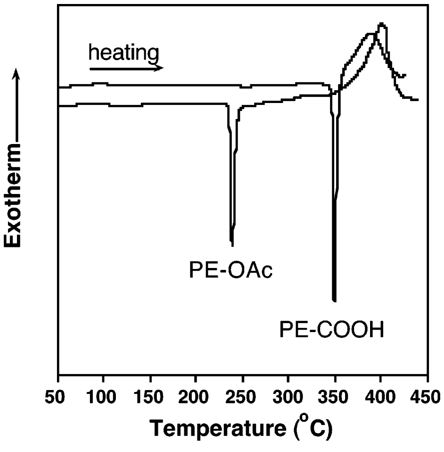


Figure 1. DSC traces of the **PE-COOH** and **PE-OAc** reactive end groups, first heat, recorded at 10 °C·min^{-1}.

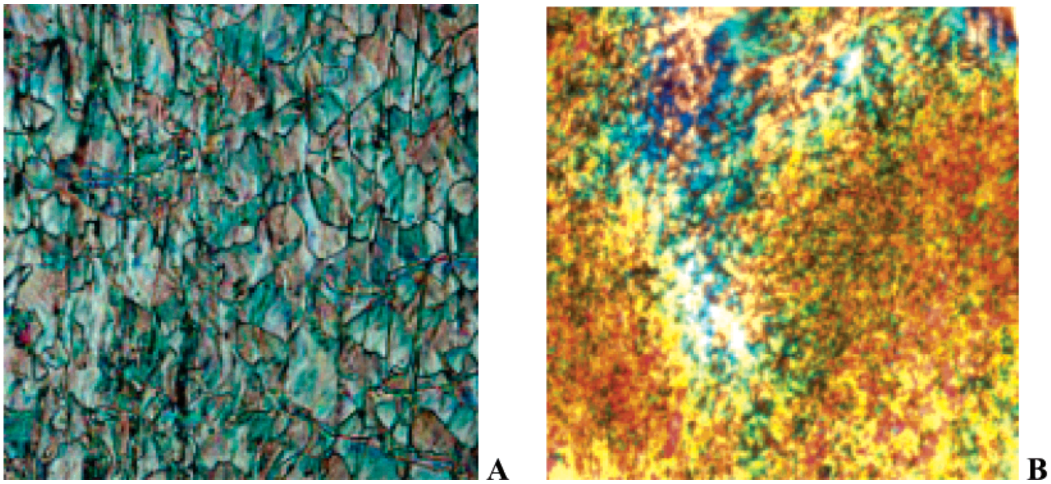


Figure 2. Microphotographs of the 1000 g mol^{-1} oligomer, HBA/HNA (73/27), between cross polarizers (20×): (A) low viscosity nematic, threaded Schlieren texture at 370 °C; (B) nematic thermoset after a 1 h cure at 370 °C.

we could estimate a value for M_v using the Mark−Houwink equation.[18] The results of the first series, where we varied the molecular weight of the reactive oligomers, are summarized in Table 2.

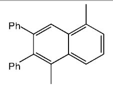
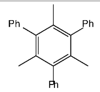
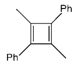
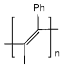
All oligomers dissolved slowly in PFP at 60 °C and formed clear solutions, confirming once more that no cross-linking has taken place during the melt polymerization process. The calculated M_v data, as presented in Table 2, appear to match well with the targeted M_n values. We want to emphasize, however, that the reported values were calculated from inherent viscosity data and should be considered indicative.

The reactive oligomer series, where we varied the HBA/HNA backbone composition, appeared more difficult to dissolve. The extreme monomer concentrations, 95 mol % HBA or HNA, did not dissolve at all and no inherent viscosity measurements could be performed. The viscosity and calculated M_v values for this series are summarized in Table 3. Again, the M_v values appear to be in good agreement with the targeted molecular weights.

Polarizing Optical Microscopy. We used hot-stage optical microscopy to study the melt behavior of the reactive liquid crystal oligomers and to gain insight into the phase type and phase stability as a function of the temperature. Both series form upon heating classic, low viscosity, nematic Schlieren textures, which is indicative of a mesophase where the molecules show long-range order but lack positional order.[20] The nematic textures are identical as observed for commercially available high molecular weight HBA/HNA polymers without reactive end groups such as Vectra.[5,17,19] When the samples were cured for 1 h at 370 °C, the nematic melt became more viscous, and after 45 min, the melt solidified completely, resulting in a fixed nematic texture. The oligomer composition and oligomer length appears to have no effect on the mesophase stability or phase type. For example our 1000 g mol^{-1} oligomer, which contains on average about 6 repeat units, shows a stable nematic phase and the nematic−isotropic transition could only be observed around 500 °C when we applied a heating rate of 100 °C·min^{-1}. None of the other investigated liquid crystalline oligomers show N−I transitions. Figure 2 shows the nematic textures of the 1000 g mol^{-1} oligomer before and after curing. Both textures are representative for the other materials as well.

The presence of the imide-based phenylethynyl end groups appears to have no effect on the phase type. From literature it is well-known that introducing all aromatic imide functionalities into liquid crystals may result in the formation of smectic phases due to the strong imide−imide interactions.[21,22] The 1000 g mol^{-1} oligomer effectively contains 21 mol % imide based end groups but no smectic phases could be observed.

Table 4. Proposed Cure Products of Phenylethynyl End-Group Chemistry[23]

Chain extension functionality	Crosslinking functionality
 Naphthalene-based cyclodimer	 Cyclotrimer
 Cyclobutadiene cyclodimer	 Polyene

An important observation is the fact that the chain extension and cross-linking chemistry associated with the phenylethynyl end groups does not, in any way, seem to interfere with mesophase formation and this strongly suggests that most of the formed functionalities maintain some sort of a linear progression. This observation is supported by recent solid-state NMR studies were ^{13}C-enriched phenylethynyl model compounds were used to identify the cured products.[23] This study, by Roberts et al., showed that depending on concentration and temperature, phenylethynyl forms chain extension (e.g., cyclobutadiene cyclodimers, and 1,5-substituted naphthalenes) and cross-linking functionalities (e.g., 1,3,5-trisubstituted benzenes, and polyenes), see Table 4.

Low molecular weight reactive oligomers, e.g. 1000 g mol^{-1} tend to form a higher concentration of trifunctional cross-links as compared to their high molecular weight counterparts, e.g. 9000 g mol^{-1}, where chain extension appears to be the dominating chemistry. The fact that trifunctional cross-links can be compatible with mesophase formation was also observed by Ober and co-workers in a series of 1,3,5-triazine-linked all-aromatic LC thermosets.[24]

X-ray Diffraction Analysis. In addition to the POM observations, we used XRD analysis to confirm the nematic nature of the cross-linked nematic thermoset samples. We prepared an aligned film of our 1000 g mol^{-1} reactive co-polyester, LCR-**1k**, by shearing the nematic melt and cross-linking the sample for 1 h at 370 °C. This film was cooled to room temperature and used for XRD analysis. Figure 3a shows the diffraction pattern as recorded at room temperature. The XRD experiment revealed a typical scattering pattern, characteristic for aligned nematic polymers. The lateral intermolecular spacing was

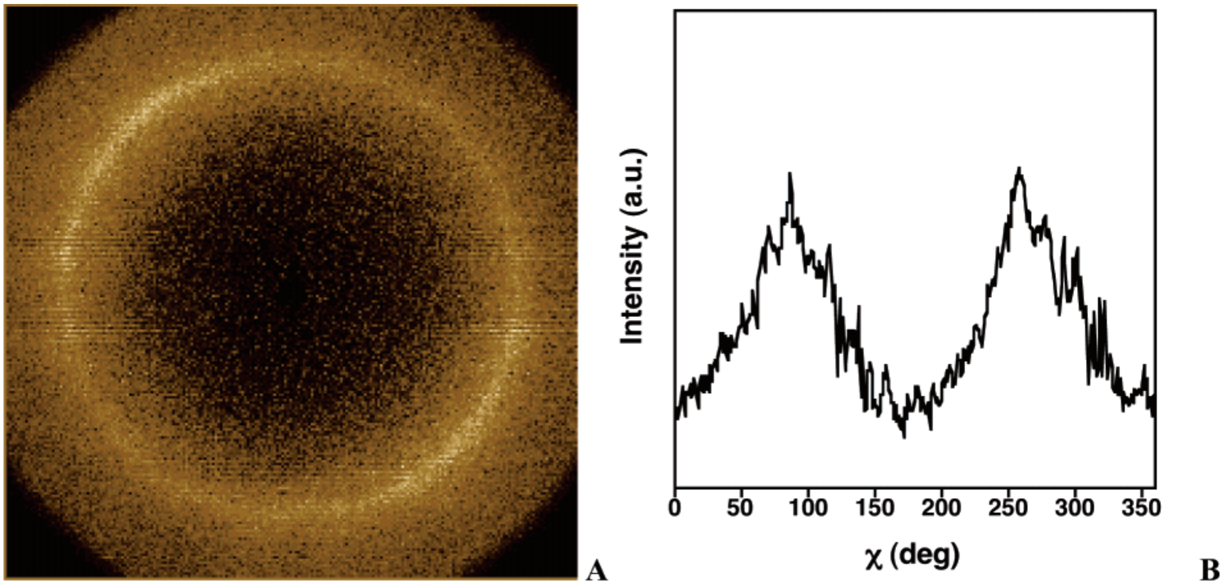


Figure 3. (A) X-ray diffraction pattern and (B) the intensity plot of an aligned and cross-linked nematic film measured at 24 °C. The film was prepared by shearing a 1000 g mol^{-1} oligomer, HBA/HNA (73/27), and cross-linking the film for 1 h at 370 °C.

measured to be 4.7 Å, which is a common value for nematic systems.

Scattering data on the 2-D detector was integrated on the 2 − θ direction over a ring containing the scattering peaks, resulting in a scattering intensity as a function of the azimuthal angle, χ, (Figure 3b). A bimodal Maier−Saupe function, eq 1, was used to fit the obtained curve in order to extract the two peak positions, χ_1 and χ_2 and widths, α_1 and α_2.[25] In this expression, i_0 is an arbitrary baseline:

$$i(\chi) = i_0 + A_1 \exp(\alpha_1 \cos^2(\chi - \chi_1)) + A_2 \exp(\alpha_2 \cos^2(\chi - \chi_2)) \quad (1)$$

From the peak width α values, obtained from the fitting of the peaks of Figure 3b with eq 1, one can easily calculate the value for the experimental order parameter, S_{exp} that can be defined in the present case, as a product of two contributions:[26]

$$S_{\text{exp}} = \langle P_2 \rangle \overline{P_2} = \overline{\langle P_2 \rangle} \quad (2)$$

where $\langle P_2 \rangle$ is the local molecular order parameter and $\overline{P_2}$ is the macroscopic director order parameter. From the α parameter, the average orientational order parameter $\overline{\langle P_2 \rangle}$ is determined using

$$\overline{\langle P_2 \rangle} = \frac{\int_{-1}^{1} P_2(\cos\beta) e^{\alpha} \cos^2\beta \, d(\cos\beta)}{\int_{-1}^{1} e^{\alpha} \cos^2\beta \, d(\cos\beta)} \quad (3)$$

where $P_2(\cos\beta)$ is de second-order Legendre polynomial of $\cos(\beta)$:

$$P_2(\cos\varphi) = \frac{1}{2}(3\cos^2\varphi - 1) \; P_2(\cos\beta) = \frac{1}{2}(3\cos^2\beta - 1) \quad (4)$$

This procedure, described in detail elsewhere,[25] reveals a nematic order parameter, $\langle P_2 \rangle$, of 0.21. Although this order parameter is small, it shows that by shearing the low viscosity nematic melt a small degree of orientation can be maintained during the 1 h curing process at 370 °C. To the best of our knowledge this is the first example of an aligned all-aromatic LC thermoset.

Table 5. Thermal Properties of the Liquid Crystalline Reactive Oligomers and Their Cured Polymers, Where Both DSC and TGA Data Were Collected Using a Heating Rate of 10 °C·min^{-1}

oligomer	T_g (°C)[a]	T_m (°C)[b]	T_d (°C)[c] in air	T_d (°C)[c] in N_2	char yield (wt %)[d]
LCR-**1k**	97	220	484	491	63
LCR-**5k**	93	245	492	498	54
LCR-**9k**	99	283	496	503	54
LCR-**13k**	96	277	494	498	54
LCR-**30k**	87	290	492	496	54
05-LCR-**5k**	148	299	493	505	58
20-LCR-**5k**	118	277	492	495	57
35-LCR-**5k**	112	263	494	497	57
50-LCR-**5k**	106	218	489	493	57
65-LCR-**5k**	109	250	491	495	56
80-LCR-**5k**	112	257	480	496	54
95-LCR-**5k**	136	340	488	500	53

[a] The glass transition (T_g) as measured by DSC on the first heat only. [b] The onset melt-temperature as measured by DSC prior to curing. [c] Sample cured for 1 h at 370 °C. Decomposition temperature measured at 5% weight loss. [d] Char yield at 600 °C of samples investigated under nitrogen atmosphere.

Dynamic Thermogravimetric Analysis. The thermal stability of the nematic polymers were determined using samples that were cured for 1 h at 370 °C in a nitrogen atmosphere. The decomposition temperatures, the temperature at which 5% weight loss occurred using a heating rate of 10 °C·min^{-1}, and the char yields for the oligomer series are summarized in Table 5. Samples were investigated in both air and nitrogen atmosphere.

The dynamic thermogravimetric experiments showed that all samples exhibit excellent thermal stabilities in both air and nitrogen environments and T_d are typically around 495 °C. There appears to be no, or little, difference between the cured polymers and the non end-capped, high-molecular weight reference material (LCR-**30k**). In fact, the end group concentration and ratio of the HBA and HNA monomers does not appear to have any influence on the thermal stability of the cured oligomers at all. These results suggest that polymer decomposition is a direct consequence of the backbone composition, and that the use of phenylethynyl has no effect on the thermal stability of the polymers. One exception has to be noted, however, and that is

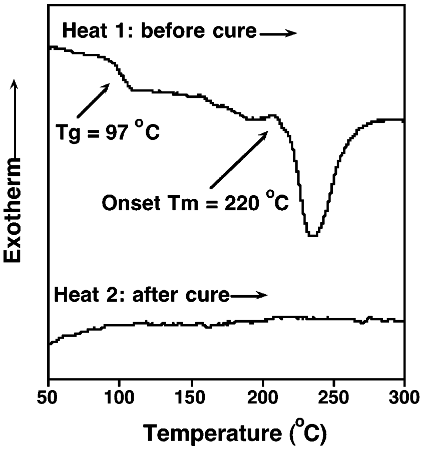


Figure 4. DSC trace of the 1000 g mol^{-1} oligomer with a backbone composition of 73 mol % HBA and 27 mol % HNA, measured at a heating rate of 10 °C·min^{-1}. The upper trace represents the first heat and the lower trace shows the second heat after curing the reactive oligomer for 1 h at 370 °C.

the 1000 g mol^{-1} sample (LCR-**1k**), which shows a somewhat higher char yield and this is believed to be due to the higher imide content.

DSC Analysis. The melt and cure behavior of the reactive liquid crystal oligomers was investigated using differential scanning calorimetry. Samples were heated using a heating rate of 10 °C·min^{-1} and held at 370 °C for 1 h to allow the resin to fully cross-link. The DSC results are summarized in Table 5 and a representative DSC trace, of the 1000 g mol^{-1} sample (LCR-**1k**), is displayed in Figure 4.

The incorporation of monofunctional end groups limits the molecular weight of the polymer and has a direct effect on properties such as the glass-transition temperature (T_g) and melt temperature (T_m). All reactive oligomers investigated by us show a T_g and T_m upon the first heat only. None of the reactive oligomers show a reaction exotherm. After cure, however, no thermal transitions could be detected by DSC, which indicated that fully amorphous nematic polymers were obtained. It was, however, not possible to reveal the T_g in the fully cured thermosets by DSC. The relation between molecular weight, backbone composition and the T_g and T_m is summarized in Figure 5 below.

Figure 5a shows the dependence of the T_g and T_m as a function of the oligomer molecular weight. For this series, the T_g does not show a strong dependence on molecular weight and shows an average value of 95 °C, which is close to the reported literature value of this polymer.[19] The T_m, on the other hand, drops significantly for oligomers with a molecular weight of 9000 g mol^{-1} or less. The T_m of the 1000 g mol^{-1} reactive oligomer, for example, drops about 70 °C as compared to its high-molecular counterpart, LCR-**30k**. The suppression of the T_m, by limiting the molecular weight of the oligomers, enabled us to successfully synthesize oligomers with either high, i.e. 95 mol %, HBA or HNA monomer ratios. Previous attempts to synthesize LCPs with monomer ratios as high as 85 mol % HBA or HNA failed because the rigid character of such polymers resulted in intractable materials.[19] The dependence of the T_g and T_m as a function of the HBA/HNA concentration is shown in Figure 5b. In this series, all oligomers have a target molecular weight of 5000 g mol^{-1} and the T_g and T_m values increase significantly when the HBA or HNA concentration exceeds 80 mol %. For example, the T_g of 05-LCR-**5k**, a 5000 g mol^{-1} oligomer with a backbone composition of 5 mol % HBA and 95 mol % HNA, displays a T_g of 148 °C, which is an increase of approximately 50 °C over the high molecular weight parent compound without reactive end groups, LCR-**30k**.

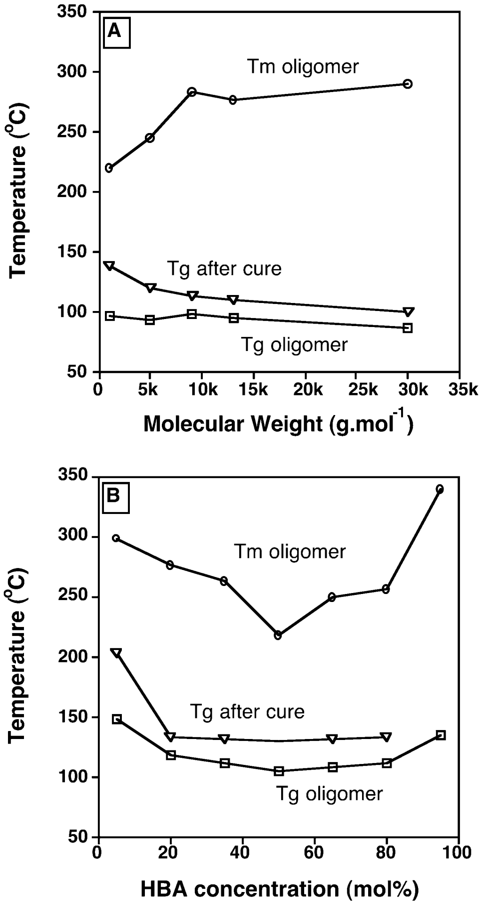


Figure 5. (A) T_g, before (□) and after cure (▽), and T_m (○) plotted as a function of the oligomer molecular weight (M_n). (B) T_g, before (□) and after cure (▽), and T_m (○) as a function of the backbone composition, i.e., varying HBA/HNA ratio.

Table 6. Complex Melt-Viscosities $|\eta^*|$ for Both Series Reactive Oligomers, Where the First Column Shows $|\eta^*|$ after a 30 min Isothermal Hold at 300 °C and the Second Columns Shows the Lowest Measured $|\eta^*|$

oligomer	$|\eta^*|$ (Pa·s)[a] isothermal hold	min $|\eta^*|$ (Pa·s)
LCR-**1k**	1	1 (349 °C)
LCR-**5k**	3	2 (365 °C)
LCR-**9k**	68	18 (370 °C)
LCR-**13k**	320	156 (370 °C)
LCR-**30k**[b]	446	172 (300 °C)
05-LCR-**5k**		
20-LCR-**5k**	3184	132 (370 °C)
35-LCR-**5k**	19	8 (359 °C)
50-LCR-**5k**	3	1 (354 °C)
65-LCR-**5k**	147	63 (370 °C)
80-LCR-**5k**	1790	131 (370 °C)
95-LCR-**5k**		

[a] The complex melt-viscosity measured after heating 30 min at 300 °C.
[b] Reference polymer without reactive end groups.

Rheology. To investigate the melt stability and cross-link behavior of the oligomers, and the effects of oligomer molecular weight and molecular composition on the complex melt-viscosity $|\eta^*|$, we conducted several rheology experiments. Pressed powder disks of the reactive oligomers were held isothermally at 300 °C for 30 min followed by heating the samples to 371 °C. The melt viscosity data are listed in Table 6.

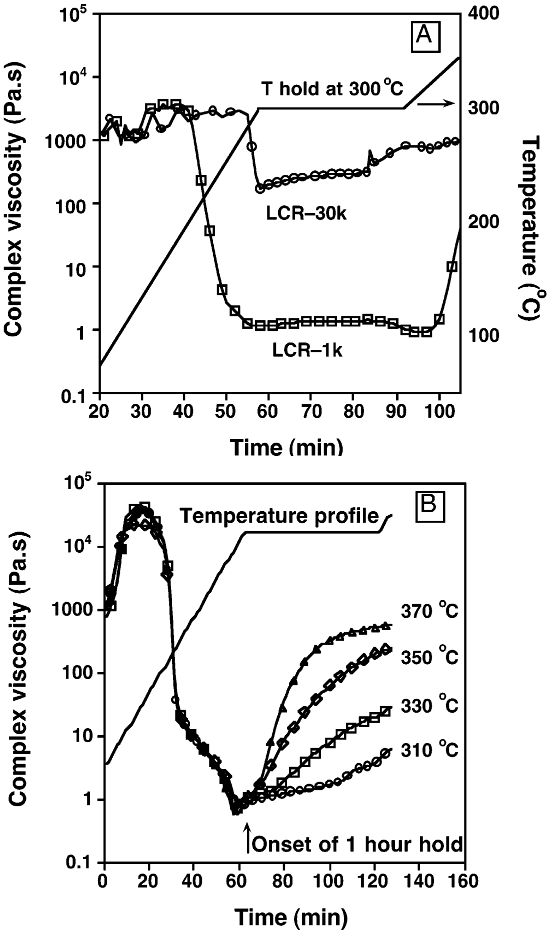


Figure 6. (A) Complex melt-viscosities ($|\eta^*|$) for LCR-**1k** (□) and LCR-**30k** (○) as a function of temperature and a 30 min hold. (B) Complex melt-viscosities ($|\eta^*|$) for LCR-**9k** as a function of different isothermal hold temperatures (1 h). Experiments were performed using a frequency of 100 rad·s^{-1} and a heating rate of 4 °C·min^{-1}.

All reactive oligomers showed stable melt viscosities during the isothermal hold. Figure 6a shows representative examples of melt viscosity curves of LCR-**1k** and LCR-**30k**.

As can be anticipated, the 1000 g mol^{-1} oligomer, LCR-**1k**, shows a significant reduction in melt viscosity as compared to the high molecular weight reference sample, LCR-**30k**. The reactive end groups remain latent during the isothermal hold but when the temperature is increased to 371 °C, the viscosity increases rapidly due to chain extension and cross-linking of the phenylethynyl end groups. In the series where we varied the HBA/HNA backbone composition, as summarized in Table 6, the complex melt viscosity of the high HBA or HNA ratio oligomers, i.e., 05-LCR-**5k** and 95-LCR-**5k**, could not be measured due to the high melting and low melt flow of the samples.

The complex melt viscosity of LCR-**9k** was also studied as a function of different isothermal holds and the results are shown in Figure 6b. Samples where heated to 310, 330, 350, and 370 °C respectively, and held at this temperature for 1 h under a nitrogen atmosphere. The rate of chain extension is slow during the 1 h hold at 310 °C but when the hold temperature increases, chain extension reactions of the reactive end groups proceeds faster as well. When a sample was cured at 370 °C, the chemistry appears to be complete after 60 min.

Dynamic Mechanical Thermal Analysis. The mechanical properties of unaligned nematic cured films were examined in the temperature range −100 °C to 500 °C at 1 Hz. The results are summarized in Table 7 and shown in Figure 7.

Table 7. Storage Modulus (E') and T_g Data of the Fully Cured LCP Films as determined by dynamic mechanical thermal analysis (DMTA)[a]

thermoset	E' (GPa) at 24 °C	E' (GPa) at 100 °C	E' (GPa) at 200 °C	T_g (°C)
LCR-**1k**	5.2	2.9	0.5	138
LCR-**5k**	3.5	1.4	0.1	120
LCR-**9k**	3.2	1.2	0.1	113
LCR-**13k**	3.9	1.4	0.1	111
LCR-**30k**	4.3	1.4	0.3	101
05-LCR-**5k**	5.2	3.1	0.9	203
20-LCR-**5k**	5.0	2.2	0.2	134
35-LCR-**5k**	5.0	2.1	0.1	132
50-LCR-**5k**	3.9	1.5		130
65-LCR-**5k**	4.9	1.8		132
80-LCR-**5k**	4.1	1.7	0.3	133
95-LCR-**5k**[b]				

[a] The measurements were conducted at a frequency of 1 Hz and a heating rate of 2 °C·min^{-1}. [b] Film too brittle to handle.

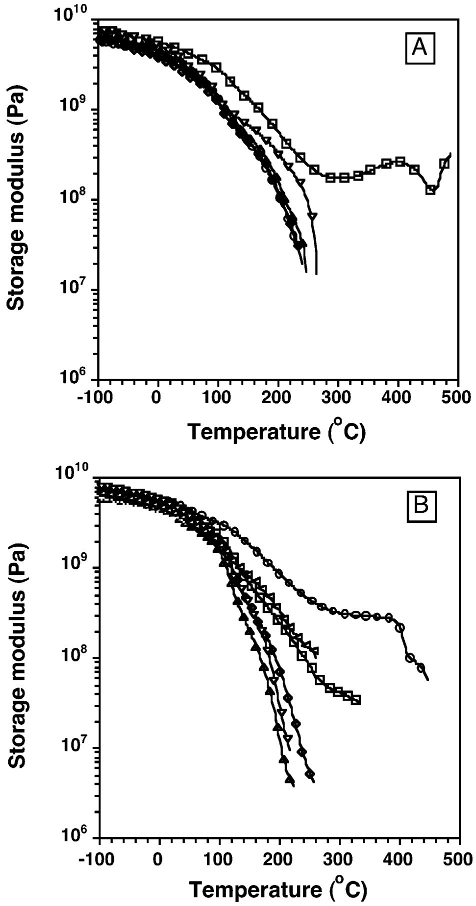


Figure 7. (A) storage modulus (E') of the cured oligomer films with different molecular weights as measured by DMTA: (□) LCR-**1k**, (▽) LCR-**5k**, (◇) LCR-**9k**, (△) LCR-**13k**, and (○) LCR-**30k**. (B) Storage modulus (E') measured by DMTA for cured oligomer films with different HBA/HNA backbone compositions: (○) 05-LCR-**5k**, (□) 20-LCR-**5k**, (◇) 35-LCR-**5k**, (△) 50-LCR-**5k**, (○) 65-LCR-**5k**, and (triangle pointing left) 80-LCR-**5k**. All measurements were conducted at a frequency of 1 Hz, while heating at 2 °C·min^{-1}.

Figure 7a shows the storage modulus (E') as a function of temperature for the molecular weight series. The molecular weight of the precursor oligomer seems to have little to no effect on the E' of the final cured film. These results support the idea that the phenylethynyl functionality tends to chain extend rather than to cross-link.[23] The 1000 g mol^{-1} sample (LCR-**1k**), however, shows an increase in E' over the whole temperature range and what appears to be a rubber plateau ranging from 300 to 500 °C, which is consistent with the thermomechanical behavior of a thermoset. Although it was reported that reactive oligomers with a high concentration of phenylethynyl produce films with a higher cross-link density, one also has to consider the fact that the LCR-**1k** sample has a high concentration of imide functionalities in the polymer backbone, which would technically define it as a polyesterimide. So the change in backbone chemistry could also in part account for the observed increase in E'.

In the series where we varied the backbone composition of a 5000 g mol^{-1} oligomer, shown in Figure 7b, we observed a different trend. The compositions high in either HBA or HNA (>80 mol %) show a distinct increase in E' over the whole temperature range. This can be understood when one considers the fact that the stiffness of the polymer backbone increases significantly when the polymer backbone resembles more and more the chemical composition of HBA or HNA homo polymers.

The T_g values of the fully cured nematic LCP films, of the molecular weight series and the HBA/HNA backbone composition series, were taken at the maximum of tan δ and listed in Table 7. Here it becomes evident that this reactive oligomer approach can offer some distinct advantages over classic main-chain chemistries. LCR-**1k**, for example, shows a T_g of 138 °C, an increase of approximately 40 °C over its main-chain, un-cross-linked counterpart, LCR-**30k**. Modifying the backbone composition toward high HNA concentrations, as is the case for 05-LCR-**5k**, 95 mol % HNA, results in a T_g of 203 °C. The T_g values of both series are also plotted in Figure 5.

Conclusions and Concluding Remarks. We have synthesized and characterized new all-aromatic main-chain liquid crystalline oligomers build around 4-hydroxybenzoic acid (HBA), 6-hydroxy-2-naphthoic acid (HNA), and reactive phenylethynyl end groups in excellent yields. The phenylethynyl functionality remains latent during the polymerization process and can be used in a later, high-temperature treatment step, to form chain extension and cross-linking functionalities. This chemistry does not, in any way, interfere with mesophase formation, and in all examples the oligomers form nematic polymers after curing. Low molecular weight oligomers, i.e., M_n < 5000 g mol^{-1}, tend to form nematic thermosets after curing, while oligomers with M_n > 5000 g mol^{-1}, polymerize predominantly via chain extension. Thermogravimetric analysis results show that all cured polymers exhibit thermal stabilities up to 490 °C in both air and nitrogen. Varying the molecular weight of the reactive oligomers, or the backbone monomer ratios, allowed us to tailor a wide range of desirable processing, mechanical and physical properties. All oligomers show stable melt viscosities, ranging from 1 to 3183 Pa·s at 100 rad·s^{-1} for at least 30 min, and the reactive oligomers may be polymerized between 310 and 370 °C. Fully cross-linked films from a 1000 g mol^{-1} oligomer precursor, LCR-**1k**, shows a T_g of 138 °C, which is an increase of 37 °C over their high-molecular weight counterpart without reactive end groups (LCR-**30k**). When the concentration of HBA or HNA increases, i.e., the oligomer backbone becomes more rigid; the T_g's of the cured polymers go up as well. 05-LCR-**5k**, for example, is a 5000 g mol^{-1} reactive oligomer containing 5 mol % HBA/95 mol % HNA and shows a T_g of 203 °C after cure. All cured LCP films show excellent storage moduli (E') ranging from 3.2 to 5.2 GPa.

Our findings may have practical implications as well: modification of current main-chain ester based liquid crystalline polymer formulations using this reactive oligomer concept could significantly extend their application range. We are currently exploring other all-aromatic main-chain and hyperbranched systems based on polyester, polyesteramide and polyesterimide chemistries.

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