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High-performance all-aromatic liquid crystalline esteramide-based thermosets

**Yiheng Dai[1], Xiangyu Bi[1], Theo J Dingemans[2,3]
and Qingbao Guan[1,2]**

Abstract
We have synthesized and characterized a new family of nematic all-aromatic polyesteramide thermosets based on 6-hydroxy-2-naphthoic acid (HNA), terephthalic acid (TA), and 4-acetamidophenol (AAP). In order to incorporate a high concentration of the amide-based monomer (AAP), the melt transition (T_{K-N}) and melt viscosity had to be lowered in order to maintain melt processable intermediates. Precursor thermoplastic reactive oligomers, end-capped with phenylethynyl functionalities, were prepared using standard melt condensation techniques with a target M_n of 1000–9000 g mol^{-1}. The reactive oligomers with 20–30 mol% AAP could easily be processed into films, and the films exhibit good tensile properties in terms of tensile strength (70–80 MPa) and elongation at break (7–10%). A glass transition of 191°C could be obtained when a 1000 g mol^{-1} oligomer (HNA/TA/AAP(20)–1 K) was thermally cross-linked. When the AAP concentration reaches 35 mol%, the rigidity of the backbone and the hydrogen bonding interactions are enhanced, which make HNA/TA/AAP(35) polymers difficult to process.

Introduction

All-aromatic thermotropic liquid crystalline polymers (TLCPs) offer superior barrier properties, solvent resistance, and low coefficient of thermal expansions (CTEs).[1,2] However, they display low glass transition temperatures (T_gs approximately 120°C), which have limited their use in demanding high-end applications such as composites, electronics, surface coatings, and barrier films. Another challenge has always been their high melting temperature (T_{K-N}) and high melt viscosity, which is a direct consequence of the all-aromatic, mostly *para*-substituted backbone.[3–5] Controlling the melting temperature, and thus improving the melt processability of all-aromatic TLCPs, has very important significance.

Various backbone modifications have been implemented over the years, which were aimed at increasing the T_g, reducing T_{K-N}, and improving the melt processability of the all-aromatic TLCPs. For instance, the introduction of non-aromatic bulky side-chain substitutions increases the T_g, while the thermal stability is compromised. Introducing nonlinear aromatic monomers, such as substituted naphthalenes; 2,5-thiophenes; 1,3-substituted benzenes; and ketone-, ether-, amide-, and imide-based monomers, lowers the backbone symmetry, disrupts crystallization, and

suppresses the T_{K-N}, whereas the liquid crystalline (LC) phase might be lost.[6–14] Another approach is to lower the molecular weight of the polymer backbone, that is, prepare oligomers and introduce reactive functionalities such as phenylethynyl or maleimide end groups at the chain ends

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(typically M_n of reactive oligomers = 1000–9000 g·mol^{-1}). This lowers the T_{K-N} and melt viscosity and makes it possible to process all-aromatic reactive oligomers, which are allowed to chain extend and/or cross-link in a successive high-temperature posttreatment step. This route yields polymers with good thermomechanical properties including high tensile strengths (83 MPa) and elongation at break (9%) that are otherwise not accessible.[15,16]

A well-known thermoplastic LC polyesteramide is composed of 60 mol% 6-hydroxy-2-naphthoic acid (HNA), 20 mol% terephthalic acid (TA), and 20 mol% 4-acetamidophenol (AAP), as shown in Figure 1. This polymer exhibits good thermal and mechanical properties and chemical resistance.[17,18] Considerable work has been reported on taking advantage of the thermal and mechanical properties of this polyesteramide (HNA/TA/AAP), such as blending HNA/TA/AAP with other thermoplastics or preparing HNA/TA/AAP-based "in situ" composites with polypropylene by using ionomers.[19–21] East et al. have tried to improve the processability of HNA/TA/AAP by introducing more nonlinear monomer HNA (up to 85 mol%), but the resulting polymers show an even higher melting temperature (T_{K-N} = 385°C). This can be explained by the fact that a too high molar percentage of HNA leads to the formation of intractable homopolymer of HNA (poly-HNA). Meanwhile, the T_g was lowered to 95°C.[18]

In principle, the molar proportion of amide units was deliberately kept low to avoid the formation of intractable compositions of very high T_{K-N}. However, it is anticipated that adding more amide units might improve the structure/property profile of polymers due to the increase of interchain hydrogen bonding. In the work presented herein, we combined the strategies of adding more amide units (AAP) to improve the thermomechanical properties and introducing reactive end groups (phenylethynyl) to control T_{K-N} and improve (melt) processability. A new series of reactive LC oligomers based on HNA, TA, and AAP with cross-linkable phenylethynyl end groups were prepared. We intensively investigated the effect of the concentration of amide units and reactive end groups on the processability, thermal and mechanical properties of the cured LC thermosets.

Experimental

Materials

All chemicals were obtained from the indicated sources and used as received. TA, AAP, and acetic anhydride were obtained from Aldrich (Zwijndrecht, The Netherlands), HNA was obtained from Ueno Fine Chemicals Ltd (Japan), and potassium acetate was purchased from Acros Organics (Geel, Belgium). For the end-group synthesis, 4-phenylethynylphthalic anhydride was obtained from Hangzhou Chempro Tech Co., Ltd (China). (98% purity). The synthesis of the reactive end groups, that is, *N*-(4-carboxyphenyl)-4-phenylethynylphthalimide (PE-COOH) and *N*-
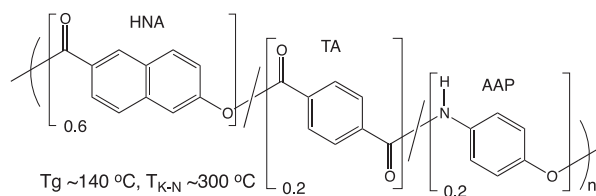
Figure 1. Molecular structure of an all-aromatic polyesteramide based on HNA, TA, and AAP.[17,18] HNA: 6-hydroxy-2-naphtoic acid; TA: terephthalic acid; AAP: 4-acetamidophenol.

(4-acetoxyphenyl)-4-phenylethynylphthalimide (PE-OAc), was reported elsewhere.[8]

Synthesis of the phenylethynyl end-capped oligomers

All reactive oligomers were synthesized using standard melt condensation techniques as shown in Figure 2. In the first series, four reactive oligomers based on HNA/TA/AAP (molar ratio of 0.6/0.2/0.2) with a target average number molecular weight M_n of 1000, 5000, and 9000 g mol^{-1} were prepared by controlling the concentration of reactive end groups using the Carothers equation.[22] The samples were labeled, HNA/TA/AAP(20)–1 K, HNA/TA/AAP(20)–5 K, and HNA/TA/AAP(20)–9 K, respectively, where HNA/TA/AAP(20) refers to the backbone composition, that is, 0.6 mol HNA, 0.2 mol TA, and 0.2 mol AAP. The integers refer to the average number molecular weight, that is, 9 K = 9000 g mol^{-1}. A reference polymer was synthesized without reactive end groups and was labeled HNA/TA/AAP(20)–Ref.

In successive series, we varied the backbone composition of a 9000 g mol^{-1} oligomer, by varying the molar ratios of HNA/TA/AAP to 0.5/0.25/0.25, 0.4/0.3/0.3, and 0.3/0.35/0.35. The samples terminated with reactive end groups were labeled HNA/TA/AAP(25)–9 K, HNA/TA/AAP(30)–9 K, and HNA/TA/AAP(35)–9 K, respectively. The reference samples for this series without reactive end groups were labeled HNA/TA/AAP(25)–Ref, HNA/TA/AAP(30)–Ref, and HNA/TA/AAP(35)–Ref, respectively.

Synthesis of HNA/TA/AAP(20)–9 K

As a representative example, we describe the synthesis of a 9000 g mol^{-1} reactive oligomer with a HNA/TA/AAP molar ratio of 0.6/0.2/0.2, labeled as HNA/TA/AAP(20)–9 K. To synthesize this oligomer, HNA (0.6 mol, 112.908 g), TA (0.2 mol, 33.226 g), AAP (0.2 mol, 30.234 g), *p*-PE-OAc (0.018 mol, 6.869 g), *p*-PE-COOH (0.018 mol, 6.617 g), and potassium acetate (0.1 mmol, 10 mg) were charged in a 250-mL three-neck round-bottomed flask. The flask was equipped with a nitrogen gas inlet, an overhead mechanical stirrer, and a reflux condenser. The reactor was purged with nitrogen for 30 min prior to the start of the reaction, and a slow nitrogen flow was maintained throughout the duration of the synthetic
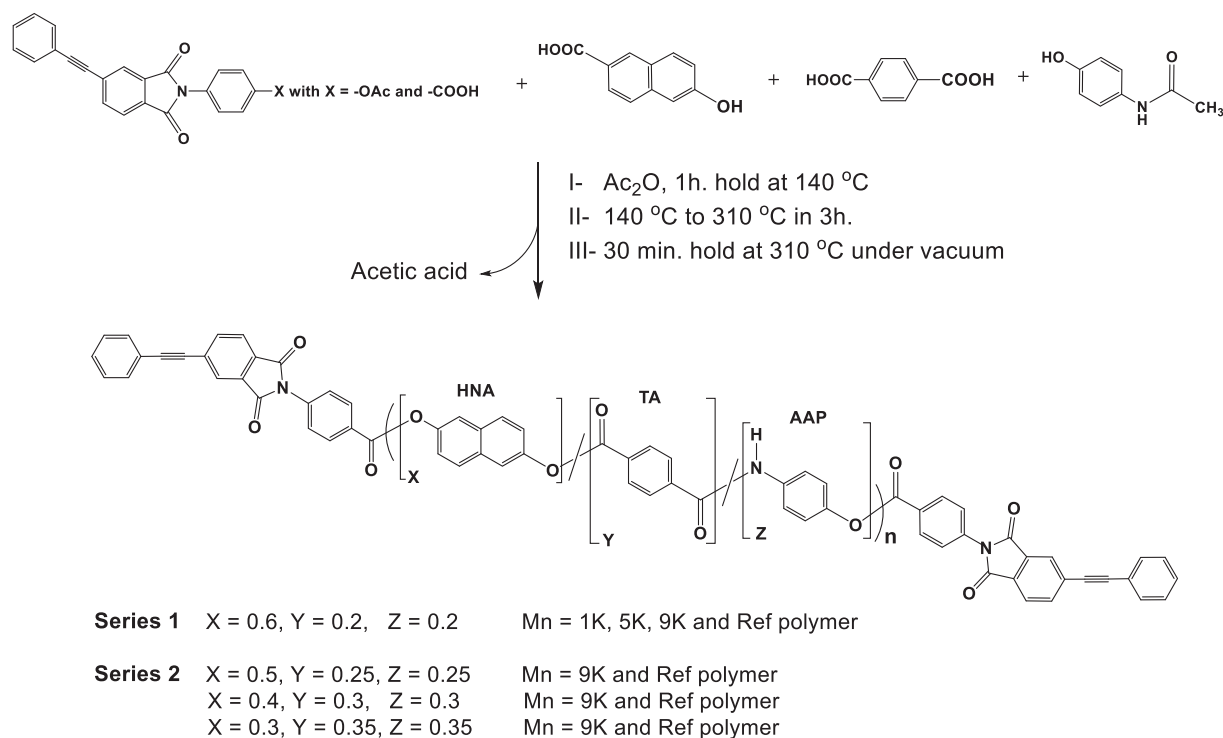
Figure 2. Synthesis and backbone of the all-aromatic LC esteramide-based reactive oligomers with phenylethynyl end groups and the reference polymers. LC: liquid crystalline.

procedure. Acetic anhydride (106 ml, 1.12 mol) was added for the in situ acetylation of the monomers. The reaction mixture was slowly stirred under 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 310°C using a heating rate of 1°C min^{-1}. During this process, acetic acid was collected as a condensation by-product. At 310°C, the nitrogen flow was stopped, and a vacuum was applied to remove the residual acetic acid and other small molecules. The reaction flask was allowed to cool down overnight under nitrogen flow, and the final product was removed from the flask and processed into a powder. A solid-state postcondensation step was performed at 250°C for 48 h under vacuum in order to remove all volatiles and ensure full polymerization. Yields for these syntheses were generally above 95%. The reference polymers were prepared under identical conditions but without PE-OAc and PE-COOH end groups.

Preparation of thin films

Melt pressed thin films were prepared using standard melt pressing techniques. The postcondensed polymer powder was placed between two Kapton™ films and consolidated in a preheated Joos hot press at 370°C for 45 min with 5 kN force. During the melt pressing step, no attempts were made to align the films.

Methods

A PerkinElmer Pyris Diamond TG/DTA (California, US) was used to study the dynamic thermal stability. The polymers were initially heated to 370°C and isothermally held at 370°C for 1 h under nitrogen to ensure full polymerization. After cooling to 25°C, the samples were analyzed using a heating rate of 10°C min^{-1} under nitrogen atmosphere.

The melt behavior of the polymers was determined by differential scanning calorimetry (DSC) using a PerkinElmer Sapphire DSC with a heating rate of 20°C min^{-1}. All measurements were conducted under nitrogen atmosphere.

A Leica DM LM optical microscope (Wetzlar, Germany) equipped with a Linkam hot stage was used to investigate the melt behavior as a function of time and temperature. The samples were investigated between glass slides upon heating using a heating rate of 50°C min^{-1}.

The rheological behavior of the polymers was investigated using a Thermo Scientific HAAKE MARS III rheometer (Germany) equipped with a force-rebalanced transducer in a parallel plate geometry. Parallel plates of 8 mm diameter were used, and samples were prepared by compression molding (8 mm in diameter and 0.2 mm thick). The samples were investigated under nitrogen atmosphere with temperature ramping (5°C min^{-1}) from 190°C to 370°C followed by an isothermal hold at that temperature for 1 h. All experiments were performed at a frequency of 1.0 Hz and a strain amplitude of 0.1%, which is well

within the linear viscoelastic range (frequency of 0.1–10 Hz and a strain amplitude of 0.001–1.0%).

Dynamic mechanical thermal analysis (DMTA) was performed with a PerkinElmer Diamond DMTA in a tension mode, using thin films $(20 \pm 0.2) \times (5 \pm 0.2) \times (0.25 \pm 0.05)$ mm^3 under nitrogen atmosphere and at a heating rate of 2°C min^{-1}. All experiments were performed at a frequency of 1.0 Hz, static tension force of 2000 mN, minimum tension force of 200 mN, tension gain of 1.5, and length amplitude of 5 μm. The minimum recordable storage modulus (E') was set to 1×10^4 Pa.

A Zwick 1445 tensile tester (Zwick GmbH, Ulm, Germany) with a 10-kN force cell was used to investigate the stress–strain behavior of the tensile specimens. All experiments were performed at 25°C at a strain rate of 1 mm min^{-1}. The data are reported as an average of five samples. The elastic modulus was measured by calculating the slope of the stress–strain curve between 0.1% and 0.3% strain.

Results and discussion

Synthesis of reactive esteramide oligomers

All oligomers with phenylethynyl end groups could be synthesized using a simple one-pot melt condensation procedure. Since the maximum polymerization temperature was 310°C, the reference polymers and reactive oligomers containing large concentrations of AAP ($\geq$30 mol%) solidified toward the end of the polymerization. The solid-state postcondensation procedure appeared very useful in this context since it ensured complete polymerization of all reactive oligomers. The oligomers were ground into a fine powder, and this powder was postcondensed at 250°C for 48 h under vacuum prior to further use.

To quantify the molecular weight of the reference polymer and reactive oligomers, we attempted to find suitable solvents or solvent mixtures, for example, dimethylacetamide, trifluoroacetic acid, and pentafluorophenol/hexafluoroisopropanol (1:1 v/v). However, all oligomers and reference polymer appeared completely insoluble at 25°C and elevated temperature, which precludes size exclusion chromatography and inherent viscosity measurements. Although it is well known that all-aromatic polyesters and polyamides are not stable in 100% sulfuric acid, we used this solvent in a final attempt to prepare polymer solutions suitable for inherent viscosity measurements. The reference polymer and reactive oligomers could be dissolved in 100% sulfuric acid; however, the inherent viscosity dropped too fast, due to backbone degradation reactions (hydrolysis), making it impossible to calculate a representative inherent viscosity.

Thermal behavior and LC phase

The thermal behavior of the reference polymers and the reactive oligomers was investigated using DSC. Figure 3
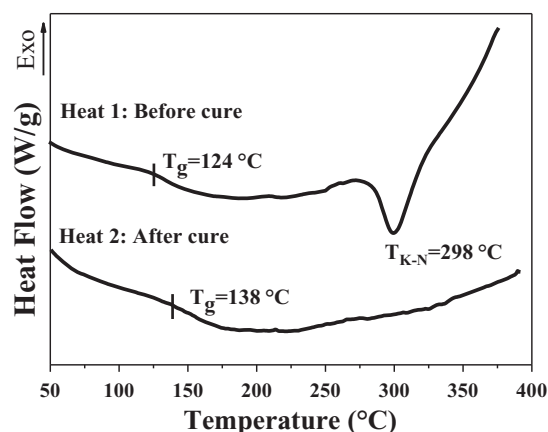
Figure 3. DSC heating trace of HNA/TA/AAP(20)–9 K after postcondensation (48 h at 250°C). Heating rate = 20°C min^{-1}/ nitrogen atmosphere. The upper trace represents the first heat, and the lower trace shows the second heat after curing the reactive oligomer for 1 h at 370°C. DSC: differential scanning calorimetry; HNA: 6-hydroxy-2-naphtoic acid; TA: terephthalic acid; AAP: 4-acetamidophenol.

depicts the first and second heating scans of HNA/TA/AAP(20)–9 K using a heating rate of 20°C min^{-1}. The first heating cycle, that is, from 25°C to 370°C, was used to detect the glass transition temperature ($T_g = 124$°C), melt transition ($T_{K-N} = 298$°C), and possibly a reaction exotherm due to the high-temperature chain extension/cross-link chemistry of the terminal phenylethynyl end groups.[23] The samples under investigation were kept at 370°C under nitrogen atmosphere for 1 h to allow the reactive oligomers to fully cure, after which the samples were quenched to 25°C and heated again. Only a T_g at 138°C is observed upon the second heat, indicating that the chain extension and cross-linking are taking place during the 1-h hold. The thermal properties of the polyesteramides are summarized in Table 1.

With regard to the reference polymers, no clearly identifiable T_g, but a broad T_{K-N} is observed upon the first heat. With an increase in AAP concentration from 20 mol% to 35 mol%, the T_{K-N} of the reference polymers shows a dramatic increase from 316°C to 396°C (Figure 4) because the ester segments are replaced by the amide segments, resulting in an increase in intermolecular hydrogen bonding interactions as expected. The incorporation of phenylethynyl end groups limits the molecular weight of the polymer and reduces the T_{K-N} values when compared to the reference polymer. For example, HNA/TA/AAP(20)–1 K shows T_{K-N} at 255°C, which is approximately 60°C lower than that of HNA/TA/AAP(20)–Ref.

In order to understand the phase behavior in more detail, we investigated the reference polymer and reactive oligomers using hot-stage optical microscopy. All reference polymers and reactive oligomers display classic nematic textures over a broad temperature range. No smectic or

**Table 1.** Thermal properties of the reactive oligomers and their cured thermosets.

Sample	$T_{K\text{-}N}$ (°C)[a]	T_g (°C)[b]	E' (GPa) at 24°C	$T_d^{5\%}$ (°C)[c]	Char yield (wt%)[c]
HNA/TA/AAP(20)–Ref	316	143	10	474	58.0
HNA/TA/AAP(20)–9 K	298	149	4.5	473	60.2
HNA/TA/AAP(20)–5 K	280	154	5.4	471	61.0
HNA/TA/AAP(20)–1 K	255	191	3.2	479	69.0
HNA/TA/AAP(25)–Ref	331	154	22	464	57.1
HNA/TA/AAP(30)–Ref	371	166	18	466	60.0
HNA/TA/AAP(35)–Ref	396	162	5.7	471	55.7
HNA/TA/AAP(25)–9 K	301	157	12	471	59.8
HNA/TA/AAP(30)–9 K	357	170	5.2	469	58.7
HNA/TA/AAP(35)–9 K	376	172	6.3	471	55.9

HNA: 6-hydroxy-2-naphtoic acid; TA: terephthalic acid; AAP: 4-acetamidophenol; DSC: differential scanning calorimetry; DMTA: dynamic mechanical thermal analysis; TGA: thermogravimetric analysis.
[a]$T_{K\text{-}N}$ data were obtained from the first heating scan of DSC experiments. Heating rate is 20°C min^{-1}/nitrogen atmosphere.
[b]T_g data were obtained from DMTA experiments using cross-linked films, defined by the maximum of the loss modulus (E'') peak. Heating rate is 2°C min^{-1}/nitrogen atmosphere and the frequency is 1 Hz.
[c]Thermal stability was evaluated using dynamic TGA. Char yield at 600°C. The sample was cured by isothermal holding at 370°C for 1 h before the measurement. Heating rate is 10°C min^{-1}/nitrogen atmosphere.
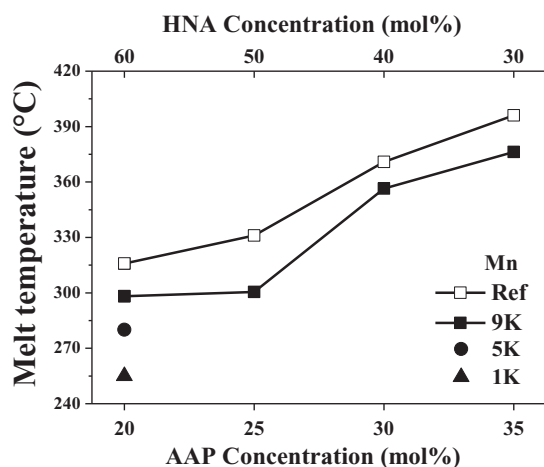

Figure 4. Melt transitions ($T_{K\text{-}N}$) of the polyesteramides reference polymers and reactive oligomers as function of the AAP (or HNA) concentration. Heating rate = 20°C min^{-1}/nitrogen atmosphere. AAP: 4-acetamidophenol; HNA: 6-hydroxy-2-naphtoic acid.

higher ordered LC phases could be detected. None of the reference polymers and oligomers showed a nematic-to-isotropic transition. As a representative example, the nematic texture of HNA/TA/AAP(20)–9 K, before and after cure, is shown in Figure 5. When the oligomers were heated and polymerized above 340°C, the viscosity of the melt started to increase rapidly. Figure 5(a) shows a nematic texture at 370°C. The nematic melt solidified after a 1-h isothermal hold at 370°C. At this point, a fixed nematic texture was obtained, which could not be sheared (Figure 5(b)), and the texture remained stable without any visible degradation up to 550°C, at which point the polymer started to decompose.[24]

Understanding the melt behavior of our polymers is critical in terms of defining the processing window. The complex melt viscosity ($|\eta^*|$) of the reference polymer and reactive oligomers as function of temperature and time was measured using a rheometer. Figure 6 shows that HNA/TA/AAP(20)–Ref has an acceptable processing window of approximately 15 min at 370°C. Its melt viscosity drops rapidly at 300°C and reaches a minimum value (1.5×10^5 Pa·s) at 350°C. However, the reactive oligomers have an even broader processing window. For instance, the melt viscosity of HNA/TA/AAP(20)–5 K starts to decrease at 250°C and reaches a minimum value (2×10^4 Pa·s) at 310°C.

After reaching the minimum value, the viscosity of HNA/TA/AAP(20)–Ref starts increasing and leveling off after a 20-min hold at 370°C, suggesting that transesterification and polymerization are taking place during the heating ramp and isothermal hold (effectively, postcondensing the polymer).[25] In the case of HNA/TA/AAP(20)–5 K, chain extension and cross-linking are taking place from 320°C resulting in an increase in molecular weight and hence a rapid increase in $|\eta^*|$. After a 25-min hold at 370°C, the chain extension and cross-linking chemistry are mostly complete and the viscosity levels off. Similar results were reported in the research on the cure reaction of phenylethynyl-terminated multiblock copolymer.[26] From the rheology experiments, it is clear that our reactive oligomers have a broader and more accessible processing window than that of the high-molecular weight reference polymer. An isothermal hold at 370°C for 1 h can cure the reactive oligomers to form cross-linked thermosets.

Figure 7 shows that all reference polymers and reactive oligomers have a sharp decrease in complex melt viscosity at their $T_{K\text{-}N}$, which is a very typical LC polymer melt
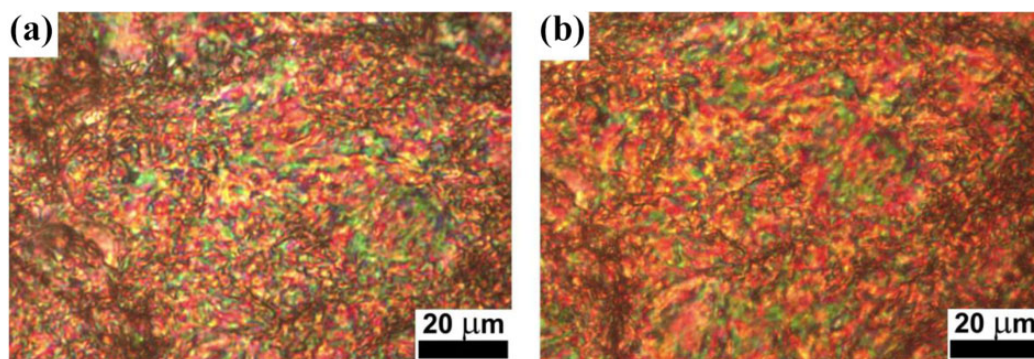
Figure 5. Microphotographs of the HNA/TA/AAP(20)–9 K melt textures (after postcondensation for 48 h at 250°C), between cross-polarizers (×100). (a) Low viscous nematic texture at 370°C. (b) Solidified nematic thermoset after a 1-h cure at 370°C. HNA: 6-hydroxy-2-naphtoic acid; TA: terephthalic acid; AAP: 4-acetamidophenol.
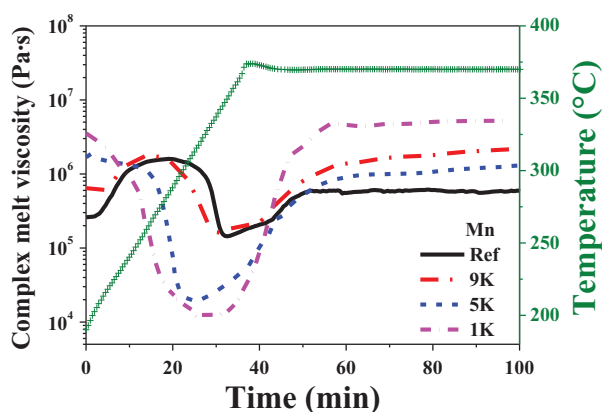
Figure 6. Complex melt viscosities ($|\eta^*|$) for the HNA/TA/AAP(20) reference polymer and reactive oligomers as function of temperature and a 1-h hold at 370°C. Experiments were performed using a frequency of 1 Hz and a heating rate of 5°C min^{-1}/nitrogen atmosphere. The test specimens were prepared after the polymers postcondensed at 250°C for 48 h. HNA: 6-hydroxy-2-naphtoic acid; TA: terephthalic acid; AAP: 4-acetamidophenol.

behavior.[27] They exhibit a broad processing window of about 20 min at 370°C and a minimum $|\eta^*|$ (approximately 1.5×10^5 Pa·s) at approximately 370°C. With the largest concentration of AAP (35 mol%), the rigidity of the backbone and the hydrogen bonding interactions are enhanced significantly; therefore, the viscosity of HNA/TA/AAP(35)–Ref and HNA/TA/AAP(35)–9 K are much higher than that of the others. This would be a good explanation for their poor mechanical property, which will be discussed later.

Thermal properties

In order to explore the thermomechanical properties of our polymers, the storage modulus (E') and loss modulus (E'') as function of temperature were studied using DMTA. Thin films of the reference polymers and cured thermosets were used for these DMTA experiments, and the results are summarized in Table 1 and Figures 8 and 9. The T_g was defined at maximum of E'' instead of the Tan δ. Reporting the T_g at the maximum of E'' is more appropriate, since this is the temperature where the polymer transits from a glassy to a rubbery state, whereas the Tan δ represents the E''/E' ratio.

Figure 8 shows that the E' (10 GPa at 24°C) of HNA/TA/AAP(20)–Ref is higher than that of the cured thermoset films. Although the reference polymer has strong hydrogen bonding interactions among the molecules, the incorporation of cross-links reduces the possibility to form such interactions. Note that the presence of cross-linked network indeed leads to a significant improvement in the thermomechanical properties of the cured films at elevated temperature. Despite the E' (3.2 GPa) of HNA/TA/AAP(20)–1 K at 24°C is smaller than that of HNA/TA/AAP(20)–Ref, HNA/TA/AAP(20)–1 K exhibits a E' of 0.8 GPa at 270°C, which is higher than that of HNA/TA/AAP(20)–Ref by a factor of 27. The phenylethynyl end groups cross-link during the curing process and form a densely cross-linked network, which typically increases the E' and T_g due to a reduction in chain mobility. Therefore, HNA/TA/AAP(20)–1 K with the largest concentration of phenylethynyl end groups displays a T_g of 191°C. However, the thermoplastic reference polymer HNA/TA/AAP(20)–Ref only has a T_g of 143°C.

Increasing the concentration of amide segment AAP from 20 mol% to 30 mol%, the T_gs and E' of the polyesteramides reference polymers and cured thermosets show a dramatic increase (Figure 9 and Table 1). This is attributed to the increase in backbone rigidity and the increased hydrogen bonding interactions, which lead to larger stiffness and less mobility of the polymer chains. For instance, the HNA/TA/AAP(30)–Ref exhibits a T_g of 166°C and E' of 18 GPa. However, the polyesteramides with 35 mol% of AAP have a slight lower T_g (160°C) and E' (approximately 6 GPa) due to the poor quality of the films.
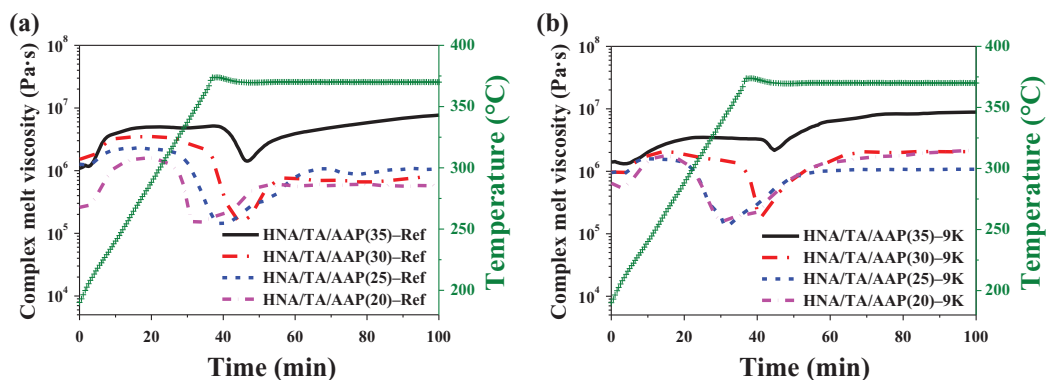
Figure 7. Complex melt viscosities ($|\eta^*|$) for the polyesteramide reference polymers (a) and reactive oligomers (b) as function of temperature and a 1-h hold at 370°C. Experiments were performed using a frequency of 1 Hz and a heating rate of 5°C min^{-1}/nitrogen atmosphere. The test specimens were prepared after the polymers postcondensed at 250°C for 48 h.
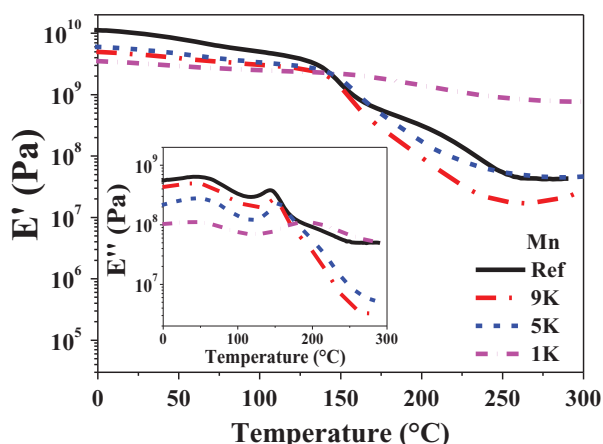
Figure 8. Storage modulus (E') as function of temperature for the HNA/TA/AAP(20) reference polymer and cured thermoset films. The inset shows the loss modulus (E'') near the glass transition. Heating rate used is 2°C min^{-1}/nitrogen atmosphere and the frequency is 1 Hz. HNA: 6-hydroxy-2-naphtoic acid; TA: terephthalic acid; AAP: 4-acetamidophenol.
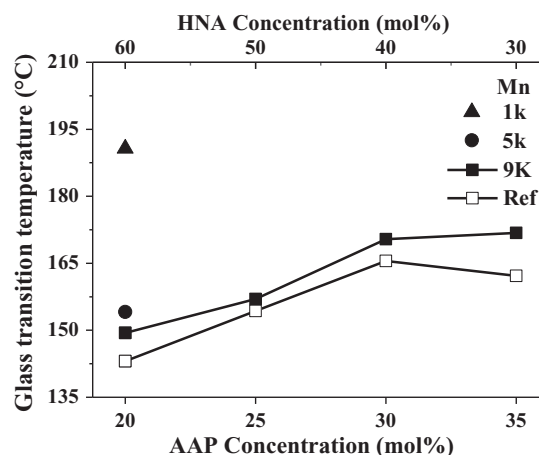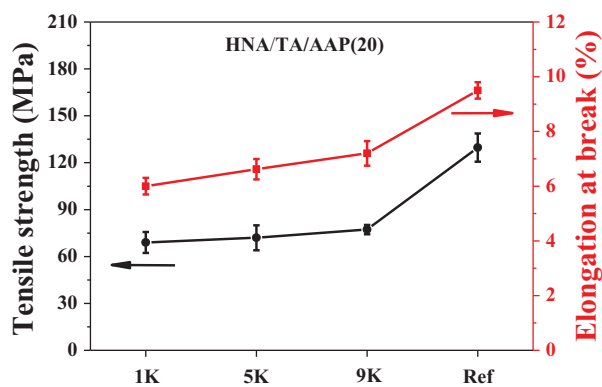

Figure 9. After cure, T_gs of the polyesteramide reference polymers and reactive oligomers plotted as function of AAP concentration. T_g data were defined at the maximum of the loss modulus (E'') peak. Heating rate is 2°C min^{-1}/nitrogen atmosphere and the frequency is 1 Hz. AAP: 4-acetamidophenol.

The thermal stability of the reference polymer and cured thermosets were evaluated using dynamic thermogravimetric analysis (TGA) at a heating rate of 10°C min^{-1}. There appeared to be no difference among the polymers with different AAP concentrations. High decomposition values ($T_d^{5\%} = 470$°C) and high char yields (60 wt%) were found, indicating that the dynamic thermal stability of these polyesteramides is comparable to that of commercial high-performance polymers such as bismaleimide and epoxy resin.[28,29] The cured HNA/TA/AAP(20)–1 K thermoset displays the best thermal stability among these polymers, which is most likely the result of a high cross-linking density. These results suggest that the thermal stability of the cured thermosets is related to the phenylethynyl reactive end-group concentration and the density of the final cross-linked network. The thermal properties of the polyesteramides are summarized in Table 1.

Tensile properties

Figure 10 shows the tensile properties of HNA/TA/AAP(20) reference polymer and cured thermoset films as function of the molecular weight of their reactive oligomers. The high-molecular weight reference polymer HNA/TA/AAP(20)–Ref shows excellent tensile properties in terms of tensile strength (135 MPa) and elongation at break (9.5%). As the molecular weight of the reactive oligomer decreases from 9000 to 1000 g mol^{-1}, the tensile properties of HNA/TA/AAP(20) thermoset films show a gradually decreasing trend. Generally, the incorporation of cross-linked network improves the stiffness of polymers but reduces the toughness, resulting in a brittle fracture behavior. For instance, HNA/TA/AAP(20)–1 K exhibits the lowest tensile strength (70 MPa) and elongation at break (6.7%) due to its highest cross-linking density.

Figure 10. The tensile properties of the HNA/TA/AAP(20) reference polymer and cured thermoset films. HNA: 6-hydroxy-2-naphtoic acid; TA: terephthalic acid; AAP: 4-acetamidophenol.

Table 2. Tensile properties of the polyesteramide reference polymers and their cured thermoset films.

Sample	Tensile strength (MPa)	Elongation at break (%)
HNA/TA/AAP(20)–Ref	130 ± 9	9.5 ± 0.3
HNA/TA/AAP(20)–9 K	77 ± 3	7.2 ± 0.4
HNA/TA/AAP(20)–5 K	72 ± 6	8.0 ± 0.4
HNA/TA/AAP(20)–1 K	69 ± 6	6.7 ± 0.3
HNA/TA/AAP(25)–Ref	106 ± 3	9.0 ± 2.1
HNA/TA/AAP(30)–Ref	83 ± 3	10.3 ± 1.0
HNA/TA/AAP(35)–Ref	38 ± 2	5.3 ± 2.6
HNA/TA/AAP(25)–9 K	64 ± 2	10.5 ± 0.9
HNA/TA/AAP(30)–9 K	69 ± 6	9.0 ± 0.7
HNA/TA/AAP(35)–9 K	45 ± 0.4	6.9 ± 1.3

HNA: 6-hydroxy-2-naphtoic acid; TA: terephthalic acid; AAP: 4-acetamidophenol.

With an increase of AAP concentration, the tensile properties of the polymers show a decreasing trend. The tensile strength and elongation at break of HNA/TA/AAP with AAP concentration less than 30 mol% were acceptable, which can be observed in Table 2. When the AAP concentration reaches 35 mol%, the rigidity of the backbone and the hydrogen bonding interactions are enhanced, which makes HNA/TA/AAP(35) polymers difficult to process. The quality of the as-pressed HNA/TA/AAP(35)–Ref and HNA/TA/AAP(35)–9 K films is poor.

Conclusions

We successfully demonstrated the synthesis of a new family of all-aromatic esteramide-based LCPs with excellent thermomechanical properties. The incorporation of phenylethynyl groups suppresses the crystal-to-nematic (T_{K-N}) transition temperature and melt viscosities of the oligomers. Rheology experiments showed that the phenylethynyl end groups extended the melting processing window

significantly for the reactive oligomers with 20–30 mol% amide-based monomer (AAP). All reactive oligomers displayed nematic mesophases, and in all cases, the nematic order was maintained after cure. Cured nematic thermoset of HNA/TA/AAP(20)–1 K exhibited outstanding thermal stability and a high glass transition temperature (191°C), which is increased by 48°C over the parent polymer HNA/TA/AAP(20)–Ref. Preliminary results showed that LCP films exhibit useful mechanical properties, that is, tensile strength (77 MPa) and elongation at break (7.2%). The chemistry presented herein will extend the thermal use range of esteramide-based LCPs.

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