



Structure and Properties of a Phenylethynyl-Terminated PMDA–Type Asymmetric Polyimide

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Abstract

A new PMR-type polyimide, designated TriA X, was investigated to determine polymer structure, processability, thermal and mechanical properties and establish the relationship between the molecular structure and those properties. TriA X is a polymerized monomeric reactant (PMR) type polyimide with an asymmetric, irregular, nonplanar backbone. Both the imide oligomers and the cross-linked polyimides of TriA X exhibited loose-packed amorphous structures, independent of thermal processing. The peculiar structures were attributed to the asymmetric backbone, which effectively prevented the formation of closed-packed chain stacking typically observed in polyimides. The imide oligomers exhibited a lower melt viscosity than a control imide oligomer (symmetric and semi-crystalline), indicating a higher chain mobility above the glass transition temperature (T_g). The cured polyimide exhibited a $T_g = 362$ °C and a decomposition temperature (T_d) = 550 °C. The cross-linked TriA X exhibited exceptional toughness and ductility (e.g., 15.1 % at 23°C) for a polyimide, which was attributed to the high molecular weight oligomer and loosepacked amorphous structure. The thermal and mechanical properties of TriA X surpass those of PMR-15 and AFR-PE-4.

Keywords





Polyimide, asymmetric structure, structure-property relationship, amorphous, processability, thermal properties, mechanical properties

1 Introduction

A new PMR-type polyimide (TriA X) is investigated to determine polymer structure, processability, and thermal and mechanical properties. This polyimide exhibits unusual characteristics that potentially overcome some of the major limitations of conventional polyimides, and thus may serve to expand service conditions and applications of both neat polyimides and associated composites. The goal of this work is to determine the relationship between molecular level structure and macroscopic properties, and thereby reach a better understanding of the behavior and characteristics of this new polyimide.

Polyimides are selected for high-temperature applications because of exceptional thermal stability and mechanical properties. These properties derive from strong interchain attractive forces involving polar interactions, aromatic π - π stacking and charge transfer complexation between dianhydride and diamine groups.¹ The intermolecular interactions effectively reduce intersegmental distance and chain mobility and increase chain rigidity, resulting in high glass transition temperature (T_g) and ultimate strength, but poor processability and toughness. Decades of effort have been devoted to development of new polyimides by tailoring molecules and adjusting interchain interactions to increase processability and toughness without sacrificing thermal properties and strength.

In 1972, NASA Lewis Research Center developed an approach to processing polyimides known as in-situ polymerization of monomeric reactants (PMR).² This technique improved the processability of polyimides compared to prior generation resin systems.³ One such PMR-type Please cite the article as: Zhang, Y., Miyauchi, M., & Nutt, S.. "Structure and properties of a phenylethynyl-terminated PMDA-type asymmetric polyimide," High Performance Polymers (2019), 31(3), 261-272, DOI: 10.1177/0954008318762592





polyimide, PMR-15, is commonly used in high-temperature composite applications. However, cured PMR-15 has a critical drawback – the resin is notoriously brittle because of a high crosslink density⁴, inevitably leading to microcracking and degradation during thermal cycling.^{5,6} This shortcoming has historically limited (but not prevented) the use of PMR-15, and since its inception a suitable alternative has been sought.

In the 1990s, NASA Langley Research Center began development of another series of polyimides with phenylethynyl terminated imide oligomers (PETI) for a Mach 2.4 high-speed civil transport (HSCT) program.⁷⁻⁹ PETI-5, one of the highly touted PETIs, is derived from 3,3',4,4'- biphenyltetracarboxclic dianhydride (BPDA), 3,4'-oxydianiline (3,4'-ODA), 1,3-bis(3- aminophenoxy)benzene (1,3-bis(3-APB)) and 4-phenylethynyl phthalic anhydride (PEPA).^{8,10} Although the phenylethynyl groups and the flexible ether linkages in the repeat units of 3,4'-ODA and 1,3-bis(3-APB) effectively improve the resin ductility, many flexible moieties in the backbone reduce the T_g (270°C) significantly compared to that of PMR-15 (341°C).^{8,11,12} Moreover, the flexible and symmetric backbone of PETI-5 lead to the formation of a semi-crystalline structure¹³, which is undesirable for composite processing.

Over the past few decades, an alternative approach to improving material properties and processability of polyimides has been explored, based on constructing polyimides from asymmetric monomers. For example, Hsiao et al. prepared a series of polyimides containing asymmetric diaryl ether segments derived from 5-(4-aminophenoxy)-1-naphthylamine, which exhibited enhanced solubility, amorphous (non-crystalline) structure, and high toughness compared to analogous polyimides based on symmetric diamines.¹⁴ Using a similar approach, Chern et al. incorporated asymmetric di-tert-butyl groups into polyimides by imidizing asymmetric diamines and various

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dianhydrides.^{15,16} The asymmetric repeat units acted to decrease intermolecular forces and reduce chain packing in the resulting polymers, resulting in high solubility, low moisture absorption, and a low dielectric constant.

A thermoset polyimide (UPILEXTM-AD) derived from 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA), 4,4'-oxydiamiline (4,4'-ODA) and PEPA was developed by Yokota et al. and commercialized by Ube Industries Ltd.^{17,18} The distorted/non-planar structure of a-BPDA inhibits intermolecular interactions, preventing dense chain stacking and increasing molecular mobility above the T_g , thereby improving processability. The asymmetric structure, however, suppresses internal rotation around the biphenyl linkage in the a-biphenyldiimide moiety, and thus the cured polymer exhibits a high T_g . Composites fabricated with this polyimide (UPILEXTM-AD) exhibit greater short-beam shear strength and flexural strength than IM7/PETI-5.¹⁸ Taking advantage of the low melt viscosity and high T_g of a-BPDA based polyimides, NASA Langley Research Center developed a polyimide for RTM liquid molding, PETI-330. PETI-330 is derived from a-BPDA, 1,3-diaminobenzene, 1,3-bis(4-aminophenoxy)benzene and PEPA, and exhibits a low complex melt viscosity (0.01–1 Pa · s) at 280°C and is stable for ≥ 2 h at this temperature.¹⁹

More recently, Miyauchi et al. developed an asymmetric polyimide derived from pyromellitic dianhydride (PMDA), 2-phenyl-4,4'-diamiodiphenyl ether (p-ODA) and PEPA.²⁰⁻²² This new polyimide system is referred to as "TriA X" for the characteristics of the polymer: *a*morphous, *a*symmetric, *a*ddition-type and *cross*-linked (\times). For the present work, a TriA X polyimide system (Figure 1a) with a 3942 g mol⁻¹ imide oligomer (*n* = 7) was selected. A distinguishing feature of TriA X is the asymmetric backbone, derived from the asymmetric monomer, p-ODA. This distinctive feature results in a disordered chain packing arrangement which profoundly affects the



behaviour of the cured polymer. For example, the loose chain packing imparts high chain mobility above the T_g , resulting in a low melt viscosity. Furthermore, the pendent phenyl group in the p-ODA moiety suppresses internal rotation around the biphenyl ether linkage and thus increases backbone rigidity, resulting in a $T_g = 362^{\circ}$ C and high material stiffness. To demonstrate the attributes and properties of TriA X that derive from the asymmetric backbone, a control material consisting of a symmetric polyimide (Figure 1b) was prepared from PMDA, 3,4'-ODA and PEPA with n = 7 for characterization and comparison to TriA X.

M.C.Gill



Figure 1. (a) TriA X and (b) PMDA/3,4'-ODA/PEPA polyimide (control).

In this work, we will show that the asymmetric/irregular/nonplanar backbone of the polyimide molecule disrupts the dense chain stacking by decreasing interchain interactions and thereby increasing intersegmental distances, resulting in a loose-packed, amorphous structure. The loose chain packing imparts greater processability relative to the Control polyimide, and the cured polymer shows superior thermal stability, ductility, strength, and toughness, compared to PMR-15 and AFR-PE-4.

2 Materials

2.1 PMDA di-ester/p-ODA/PEPA mono-ester Monomers





A powder blend of PMDA *di*-ester/p-ODA/PEPA *mono*-ester (Kaneka, College Station, Texas, USA) was obtained and used in this study. Briefly, PMDA and PEPA were esterified in ethanol, based on the method reported by Houlihan *et al.*.²³ After PMDA and PEPA were converted to PMDA *di*-ester and PEPA *mono*-ester, p-ODA was added to the solution with ethanol and heated while stirring, yielding a PMDA *di*-ester/p-ODA/PEPA *mono*-ester solution. The stoichiometric ratios were PMDA *di*-ester: p-ODA: PEPA *mono*-ester = 7: 8: 2, forming an oligomer with a molecular weight of 3945 g mol⁻¹ via heat-triggered imidization. Monomer powder was obtained by drying monomer solution at 50°C in vacuum. The monomer was stored at room temperature prior to use.

2.2 PMDA/4,4'-ODA/PEPA Imide Oligomer

PMDA/4,4'-ODA/PEPA imide oligomer was prepared by a two-step synthesis method, in which 4,4'-ODA was dissolved and stirred in N,N-dimethylacetamide (DMAc) at room temperature for 15 min under nitrogen. A stoichiometric amount of PMDA was added to the DMAc solution, and after stirring at room temperature under nitrogen for 1 h, a stoichiometric amount of PEPA was added to the solution, and the solution was stirred at room temperature under nitrogen for 12 h. The stoichiometric ratios were PMDA: 4,4'-ODA: PEPA = 7: 8: 2, forming an amide acid oligomer with a degree of polymerization n = 7. The amide acid oligomer solution was coated onto a glass substrate and thermally imidized at 250°C for 2 h, then at 300°C for 2 min. The imide oligomer was ground using mortar and pestle, and the powder was stored at room temperature before use.

For clarity, the PMDA/4,4'-ODA/PEPA imide oligomer henceforth will be referred to as the Control imide oligomer, while the polyimide derived from PMDA/4,4'-ODA/PEPA imide oligomer will be referred as the Control polyimide (meaning Control cured imide resin).

2.3 TriA X Polyimide Panels





TriA X polyimide panels were produced from TriA X imide oligomer via compression molding. First, PMDA *di*-ester/p-ODA/PEPA *mono*-ester monomer blend was imidized at 250°C for 2 h in an oven to obtain TriA X imide oligomer (Figure 2a). The monomer blend powder melted at 130°C²⁴, and hence a 30-min dwell at 130°C was added before imidization at 250°C to allow oligomer chains to grow. The imide oligomer was subsequently ground using an electric grinder and dried at 80°C for 1 h under vacuum.

The imide oligomer powder was placed in a stainless steel frame coated with release agent on a steel sheet. Both sides of the frame were covered by polyimide release film. The oligomer powder was cured in a hot press (Figure 2b). The oligomer powder was heated to 325°C at a ramp rate of 3°C/min, and equilibrated at 325°C for 5 min to even the temperature distribution. At the end of the 325°C dwell, a two-minute bump sequence (20 bumps) was performed to evacuate volatiles, and the consolidation pressure (1.72 MPa) was subsequently applied. The panels were heated to 371°C at a rate of 3°C min⁻¹, then cured at 371°C for 2 h. After cure, the panels were cooled to room temperature under pressure at a rate of 5°C min⁻¹.



Figure 2. Molding cycle for TriA X resin: (a) oven cycle and (b) hot press cycle.



3 Experiments



3.1 X-Ray Diffraction

To investigate material structures, wide-angle X-ray diffraction (XRD) measurements of the oligomers and polyimides of TriA X and Control resin systems were conducted using an X-ray diffractometer (Ultima IV, Rigaku, Japan) with Cu-K_a incident radiation (λ =0.1541 nm). To determine the dependence of the material structure of TriA X on thermal history, a series of TriA X imide oligomers and polyimides were prepared, as described in Table 1. The thermal processes encompass two types of conditions: (a) those that favor crystallization at relatively low temperatures (200°C for imidization and 350°C for crosslinking) and slow cooling rates (1°C min⁻¹), and (b) those that do not, and feature high temperatures (250°C for imidization and 371°C for cross-linking) and rapid cooling rates (quench).²⁵ The Control polyimide was prepared by heating the Control imide oligomer at 371°C for 2 h. XRD scans were recorded at 40 kV and 44 mA at a scan speed of 3° min⁻¹. No attempt was made to ensure a constant mass of samples in the X-ray beam, so absolute intensity comparisons of the patterns from different samples was not warranted. The XRD patterns were normalized based on baselines.

Specimen name	Thermal history	Cooling rate	Degree of imidization (%)	T_g (°C)
Oligomer 1	200°C/30 min	Liquid N ₂ quench	89.6	225
Oligomer 2	200°C/30 min	1°C min ⁻¹	86.3	228
Oligomer 3	250°C/30 min	Liquid N ₂ quench	93.6	246
Oligomer 4	250°C/30 min	1°C min ⁻¹	94.6	245
Oligomer 5	200°C/2 h	Liquid N ₂ quench	91.4	230

Table 1. TriA X imide oligomers and polyimides.





Oligomer 6	200°C/2 h	1°C min ⁻¹	89.9	228
Oligomer 7	250°C/2 h	Liquid N ₂ quench	94.7	247
Oligomer 8	250°C/2 h	1°C min ⁻¹	94.8	247
Polyimide 1	250°C/2 h+350°C/2 h	Ice water quench	-	342
Polyimide 2	250°C/2 h+350°C/2 h	1°C min ⁻¹	-	338
Polyimide 3	250°C/2 h+371°C/2 h	Ice water quench	-	360
Polyimide 4	250°C/2 h+371°C/2 h	1°C min ⁻¹	-	362

3.2 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of TriA X was performed under nitrogen purge at a flow rate of 5.00 ml/min (Q5000, TA Instruments, USA). TGA data was obtained to determine degrees of imidization of the oligomers in Table 1, as well as the decomposition temperature (T_d) of TriA X cured polyimide. To remove residual solvent and moisture, the monomer blend and imide oligomers were dried at 60°C for 1 h and subsequently at 80°C for 1 h in the TGA, prior to each experiment. For TGA experiments, the monomer blend and imide oligomers were heated from 80°C to 400°C at a rate of 5°C min⁻¹. The monomers were assumed to be fully converted to imide oligomer at 400°C (no degassing was observed during TGA from 25°C to 400°C after the monomers were heated to 400°C). The degrees of imidization of the imide oligomers were determined by Equation (1), where W_0 is the percent weight loss of each oligomer, and W_M is the percent weight loss of the monomer blend, as described by Omote et al.²⁶

Degree of imidization =
$$\left(1 - \frac{W_O}{W_M}\right) \times 100\%$$
 (1)

A TriA X polyimide was prepared in the TGA by holding the monomers at 250°C for 2 h and subsequently at 371°C for 2 h. The polyimide was heated from 25°C to 650°C at a rate of 10°C min⁻

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¹. The T_d of TriA X was determined by the onset of the decomposition reaction, calculated by the intersection of lines tangent to the knee of the weight loss curve, using thermal analysis software (Universal Analysis 2000, TA Instruments, USA).

3.3 Differential Scanning Calorimetry

The values for T_g and the possibility of phase transitions in TriA X oligomers and polyimides were investigated using differential scanning calorimetry (DSC; Q5000, TA Instruments, USA). Tests were performed by heating samples from 25°C to 490°C at 10°C min⁻¹ under nitrogen purge at a flow rate of 50 ml min⁻¹.

3.4 Rheological Measurements

Rheological measurements were performed on TriA X and the Control imide oligomers using a parallel plate rheometer (AR 2000EX, TA Instruments, USA). Oligomer 8 of TriA X, which had a similar thermal history to the Control imide oligomer, was selected for rheological measurements. The oligomers were ground and pressed at room temperature into 25 mm discs, 0.9-1.1 mm thick, using a hand press (YLJ-12T, MTI, USA).

Pressed oligomer discs were placed on the stationary lower plate of the rheometer, while the upper plate was oscillated at a frequency of 1.0 Hz, and at a strain of 0.1 %. The measurements were performed at a heating rate of 3°C min⁻¹ from 225°C to 450°C. The plate gap was adjusted under a normal force control of 1 N to maintain contact with the samples. Complex viscosity ($|\eta^*|$) was determined from rheological experiments.

3.5 Mechanical Tests

The tensile and flexural properties of TriA X polyimide were measured in accordance with ASTM D638²⁷ and ASTM D6272²⁸ standards, respectively. The tests were conducted using a load Please cite the article as: Zhang, Y., Miyauchi, M., & Nutt, S.. "Structure and properties of a phenylethynyl-terminated PMDA-type asymmetric polyimide," High Performance Polymers (2019), 31(3), 261-272, DOI: 10.1177/0954008318762592





frame (5567, Instron, USA) with a 5000-N load cell (2525-805, Instron, USA). Test specimens were stored in a desiccator prior to testing.

Tensile tests were performed at a displacement rate of 1.0 mm min⁻¹ at -54°C, 23°C, 232°C and 288°C in an environmental chamber (3119-506, Instron, USA). The test temperatures were monitored by a thermocouple attached to the clamps, adjacent to test specimens. The strain at 23°C, 232°C and 288°C were measured using a 3D optical deformation measuring system (ARAMIS; Adjustable Base 2.3M, GOM, Germany). Speckle patterns were painted on the gauge sections of the specimens prior to the tests. As the specimens deformed, the measuring system tracked the speckle pattern evolution to determine dimension change. Due to moisture condensation on specimen surfaces, the stain at -54°C was measured using an extensometer (2630-121, Instron, USA). Flexural tests were performed at a strain rate of 0.1 mm mm⁻¹ min⁻¹ at 23°C with a load span of 25.5 mm and a support span of 50.7 mm. Beam deflection was measured using a deflectometer (2601-093, Instron, USA).

4 Results and Discussion

4.1 Material Structure

XRD was performed on TriA X and Control samples to characterize the material structures. The XRD patterns are shown in Figure 3, with origins shifted vertically for clarity. No sharp peaks were observed in the XRD patterns from the eight oligomers samples or the four polyimides. The twelve samples, prepared according to the thermal processes listed in Table 1, exhibited nearly identical X-ray scattering behavior, each showing broad halos at 2θ values of 6.0~6.2° and 18.0~18.3°. The absence of sharp peaks indicated amorphous (non-crystalline) structures in all TriA X oligomer and polyimide samples. In contrast, the XRD patterns from the Control imide oligomer and polyimide Please cite the article as: Zhang, Y., Miyauchi, M., & Nutt, S.. "Structure and properties of a phenylethynyl-terminated PMDA-type asymmetric polyimide," High Performance Polymers (2019), 31(3), 261-272, DOI: 10.1177/0954008318762592





displayed multiple sharp diffraction peaks at 2θ values of 6°, 15°, 22° and 26° and a scattering halo at ~20°, indicating semi-crystalline structures.



Figure 3. XRD patterns of TriA X and Control

The X-ray scattering patterns from the TriA X imide oligomers and polyimides exhibited two prominent broad halos. Using Bragg's law,

$$\lambda = 2d\,\sin\theta \tag{2}$$

where λ is the X-ray wavelength, θ is the angle at which the intensity maximum occurs, and d is the Bragg spacing, the Bragg spacings of the two halos were 0.5 nm and 1.4 nm (at $2\theta = 6.0 \sim 6.2^{\circ}$ and at $2\theta = 18.0 \sim 18.3^{\circ}$, respectively). The former spacing corresponds to a Van der Waals (VDW) distance of 0.4~0.5 nm, and the latter one indicates an interchain distance larger than Van der Waals





(LVDW).²⁹ Although the intensity of the LVDW halo was less than that of the VDW halo, the presence of the LVDW halo indicated that a portion of the chains manifest intermolecular distances greater than VDW bonds, and overall the polymers exhibited looser packing than VDW bonding. The amorphous structures with LVDW packing strongly affected the behavior of TriA X, as described in sections 4.2, 4.3 and 4.4.

DSC curves from the TriA X imide oligomers or polyimides showed no evidence of crystallization or melting (Figure 4), and only glass transition and cross-linking were observed. The cross-linking reaction peaks of the oligomers occurred at ~390°C, and the T_g 's of the oligomers and polyimides are listed in Table 1. The thermal properties of TriA X are described further in Section 4.3. The DSC results reaffirmed the absence of crystalline regions, leading to the conclusion that the TriA X imide oligomers and polyimides were entirely amorphous (non-crystalline). Moreover, the eight imide oligomers and four polyimides were prepared by different thermal processes, as described in Section 3.1. These processes included conditions favorable to crystallization (relatively low temperatures and slow cooling rates), as well as conditions that did not favor crystallization (high temperatures and rapid cooling rates).²⁵ Thus, the formation of the amorphous structure in the oligomer and polyimide samples was independent of thermal process history.







Figure 4. DSC curves of TriA X imide oligomers and polyimides.

Generally, semi-crystalline imide oligomers or polyimides are undesirable for processing of polyimide matrix composites - high temperatures are needed to melt crystalline regions, and this results in narrow processing windows.³⁰ Moreover, crystallization inhibits cross-linking, generating defects in the form of unreacted groups in remaining crystallites if crystal phases are not completely eliminated before or during cross-linking. Such defects yield reduced material toughness.^{13,31} Although some semi-crystalline polyimides can be converted to amorphous structures by controlling process parameters^{13,31}, for large-scale manufacturing of composite components, thermal gradients, particularly in large parts, are unavoidable and can yield uneven polymer structures. Thus, amorphous imide oligomers and polyimides are preferred over semi-crystalline ones, because there is no need for high temperature processing to melt crystalline regions.^{30,31}

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The ability to form completely amorphous structures in TriA X is attributed to the asymmetric backbones. In polymers, symmetric backbones and strong intermolecular interactions favor crystallization, because symmetric chains permit the regular, close packing required for crystallite formation, while strong interchain attractions stabilize orderly alignments.²⁵ Consequently, symmetric polyimides, such as AFR-PE-4³² and PETI-5¹³, tend to form semi-crystalline structures. We assert that the pendent phenyl group on the ODA moiety increases backbone irregularity by forming three repeat-unit configurations: head-to-head, head-to-tail, and tail-to-tail. In addition to the irregular geometry, the nonplanar structure of p-ODA disrupts the closed-packed arrangements of polymer chains and increases intersegmental distances, weakening interchain interactions.

The hypothesis that the asymmetric p-ODA affects the chain arrangements can be tested by investigating the polymer structure that arises when the pendent phenyl groups are absent from the polymer backbones. The Control imide oligomer and polyimide had formulated chemical structures identical to the TriA X imide oligomers and polyimides (except for the extra phenyl groups of the diamines in TriA X system). As mentioned previously, multiple sharp diffraction peaks were present in the XRD patterns of the Control imide oligomer and polyimide (Figure 3), indicating that semi-crystalline structures. Because the pendent phenyl groups were absent from the Control system, the symmetric chains were able to adjust conformations and form orderly arrangements in response to strong interchain forces. In contrast, the asymmetric/nonplanar p-ODA characteristic of the TriA X backbone yielded structures that were entirely amorphous.

4.2 Thermal Processability

Rheological measurements were performed on Oligomer 8 of TriA X and the Control imide oligomer (with similar thermal history) to investigate the effects of the asymmetric structure of p-

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ODA on the processability of the TriA X system. The $|\eta^*|$ (complex viscosity) profiles of TriA X imide oligomer and the Control imide oligomer are shown in Figure 5a. The Control imide oligomer did not soften or melt upon heating up to 450°C, displaying a constant viscosity of ~10⁵ Pa · s. The $|\eta^*|$ of the TriA X imide oligomer began to drop at 258°C, and reached a local minimum at 284°C, a characteristic of residual imidization²⁴. The minimum $|\eta^*|$ of TriA X imide oligomer (2487 Pa · s) occurred at 358°C, which was much lower than the $|\eta^*|$ of the Control imide oligomer. In addition to the viscosity difference, the processability distinction between the two oligomers was demonstrated by a change in appearance after heating. Both TriA X and the Control imide oligomers appeared as identical orange powders prior to rheological measurements (Figure 5b and 5c top). After the measurements, the TriA X imide oligomer powder deformed and fused to the metal plates, turning darker in color. In contrast, the Control imide oligomer was low enough for composite compression molding under 1.72 MPa²⁴, while the control imide oligomer was not processable. This feature of the TriA X imide oligomer was attributed to the extra phenyl group in the ODA moiety.



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Figure 5. (a) Complex viscosity |η*| profiles of TriA X imide oligomer (red solid) and the Control imide oligomer (blue dash) and images of TriA X imide oligomer (b) and Control imide oligomer (c) before (top) and after (bottom) measurements.

Because of the asymmetric backbones, TriA X imide oligomers were amorphous (noncrystalline), and polymer chains were loosely packed, allowing space for rearrangement above T_g . In contrast, the chain arrangements in the Control imide oligomer were more orderly. The strong interchain attractions held polymer chains so tightly that even at 450°C, the thermal energy was insufficient for chain movement. Consequently, the TriA X imide oligomer exhibited much lower melt viscosity than the Control imide oligomer.

4.3 Thermal Properties

The T_g 's and T_d 's of TriA X, PMR-15^{11, 33} and AFR-PE-4^{32,34} are shown in Figure 6. The T_g of TriA X was 362°C, 21°C above that of PMR-15, and 15°C above that of AFR-PE-4, while the T_d of TriA X was 130°C above that of PMR-15, and ~30°C above that of AFR-PE-4. Note that all values were determined using TGA at the same heating rate (10°C min⁻¹). Also, the T_g value of TriA X is consistent with the DSC measurements shown previously in Fig. 4 (TriA X is Polyimide 4). The T_g of the Control polyimide was not detected by DSC because of the high degree of crystallinity.





*All T_d 's were measured using TGA at a heating rate of 10°C/min.

The T_g of a polymer is affected by multiple factors. Decreases in intermolecular interaction or increases in interchain spacing both cause a reduction in T_g , while suppression of chain rotation increases chain stiffness and thus increases T_g .^{25,29} Although the increased interchain distances resulting from the asymmetric/nonplanar structure of p-ODA, tend to decrease the T_g of TriA X, the pendent phenyl group hinders the rotation of the diphenyl ether linkage in the ODA moiety, raising the internal rotation energy barrier of the backbone. Thus, the enhanced chain stiffness partially counterbalances the adverse influence of loose chain packing, resulting in a T_g of 362°C.

The superior thermal stability of TriA X compared to PMR-15 and AFR-PE-4 can be understood in terms of molecular structure. In particular, PMR-15 consists of (a) 4,4'-methylenedianiline (MDA), (b) 4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and (c) nadic anhydride (NA; end-cap). In contrast, AFR-PE-4 is derived from (a) p-phenylene diamine (PPD), (b) 4,4'hexafluoroisopropylidene diphthalic anhydride (6FDA) and (c) PEPA (end-cap). In general, PEPA-

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terminated polyimides exhibit greater thermo-oxidative stability than NA terminated polyimides.³⁵ Moreover, the methylene linkage in MDA reportedly is thermally less stable than the ether bond in ODA or p-ODA, and consequently, ODA-PMDA polyimides exhibit greater thermal stability in air and inert atmosphere than MDA-PMDA polyimides.³⁶ In addition, the fluorinated methyl group of 6FDA can be easily dissociated by the thermal cleavage of C-CF₃ bonds at high temperatures, and thus the thermal stability of linear aromatic polyimides derived from 6FDA is less than that of PMDA-based polyimides when the diamines are identical.³⁷⁻⁴⁰ Thus, the high T_d of TriA X derives from the combined effects of the backbone monomers and the PEPA end-cap.

4.4 Mechanical Properties

Mechanical tests were performed on TriA X polyimide at select temperatures, as given in Table 2. The stress-strain curves of TriA X in the tensile tests are shown in Figure 7, and the mechanical property values appear in Table 3. After an initial period of linear elastic deformation, all curves exhibited nonlinear elastic deformation prior to the yield points (zero slope in stress-strain curve). At -54°C, TriA X failed at 9.7% strain prior to reaching a yield point. Likewise, at 23°C, the polymer broke before reaching a true yield point. However, the stress-strain curve exhibited a large nonlinear region, and the rupture point (at 15.1% strain) displayed a near-zero slope (0.05 GPa). Thus, the nonlinear region at 23°C is believed to contain both elastic and plastic deformation.

Higher test temperatures resulted in lower yield strengths, but broad stress plateaus and much greater ductility. At 232°C and 288°C, TriA X yielded at 7.6 % and 3.6 % strain, with yield strengths of 39.5 MPa and 25.9 MPa, respectively. Beyond the yield points, stress first dropped slightly, then rose slowly with increasing strain, producing a broad stress plateau. The stress drop at the yield point at 288°C was more apparent than that at 232°C. Before rupture, stress increased slightly due to

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alignment of polymer chain segments. At 288°C, the speckle pattern started to detach from specimens at ~37 % strain, prior to failure. Strain beyond 37 % (red dashed line in Figure 7) at 288°C was estimated based on the displacement of the grips, recorded by the load cell. Overall, as test temperatures increased, the tensile strength and Young's modulus values decreased, while ductility increased.

Generally, highly cross-linked thermosets are brittle, displaying only linear elastic deformation in tensile tests, while the typical tensile stress-strain curve of thermoplastics exhibits linear and nonlinear elastic deformation, yielding, chain strengthening and large strain-at-failure. Although TriA X is a thermoset polymer, at high temperatures, the polymer exhibited thermoplastic-like mechanical behavior, with post-yield stress drops and extensive ductility.

Mechanical test	Test method	Temperature (°C)	Length ^a (mm)	Width ^b (mm)	Thickness ^c (mm)	Number of specimens
Tensile	ASTM D638 ²⁷	-54	65.92	3.18	3.08	10
		23	65.96	3.16	3.13	6
		232	66.03	3.17	3.11	5
		288	66.0	3.16	3.14	5
Flexural	ASTM D6272 ²⁸	23	60.76	12.7	3.15	6

Table 2. Specimens for mechanical tests.

^aTotal length of specimens.

^{b,c}Gauge section dimensions.







Figure 7.	Stress-	strain	curves	of	TriA	Х	tensile	tests.
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Temperature (°C)	Tensile modulus (GPa)	Tensile strength (MPa)	Strain-at-failure (%)	Flexural modulus (GPa)
-54	3.94 ± 0.33	153.3 ± 5.1	9.7 ± 2.1	-
23	3.57 ± 0.04	119.0 ± 1.1	15.1 ± 1.6	3.88 ± 0.05
232	1.97 ± 0.04	47.0 ± 1.8	36.5 ± 2.1	-
288	1.54 ± 0.04	36.9 ± 1.0	>37*	-

*Speckle pattern painting detached from specimens when strain was greater than 37 % so that the measured strain above 37 % was not accurate.

In flexural tests, specimens did not yield or break within the 5% strain limit specified by the test

standard²⁸. Figure 8a shows a beam specimen during a bending test at a deflection corresponding to





 ~ 10 % strain. After unloading, the specimen recovered elastically to a flat beam (Figure 8b). The exceptional elastic flexibility was notable, particularly since most polyimides are brittle.



Figure 8. TriA X specimen of flexural test: (a) in test and (b) after test.

A comparison of mechanical properties of TriA X, PMR-15⁴¹⁻⁴³ and AFR-PE-4³⁴ is shown in Figure 9. TriA X exhibited an elastic modulus similar to PMR-15 and AFR-PE-4, but with greater toughness. Toughness - the energy a material absorbs during load prior to failure, can be determined simply by the area under the tensile strain-stress curve.²⁵ When the elastic moduli of two materials are similar, greater tensile strength and/or strain-at-failure indicate greater toughness. At 23°C, the ductility of TriA X was ten times of that of PMR-15 (1.5%)³⁷ and six times of that of AFR-PE-4 (2.5%)³⁴, while the tensile strength was three times that of PMR-15 (37.2 MPa)⁴¹ and 65% greater than that of AFR-PE-4 (72.0 MPa)³⁴. At 288°C TriA X exhibited tensile strength 21% greater than PMR-15 (30.5 MPa)⁴¹.

The formulated molecular weight of the imide oligomer (3942 g mol⁻¹) was greater than that of

PMR-15 (1500 g mol⁻¹)² and AFR-PE-4 (2634 g mol⁻¹)³². Imide oligomers with greater molecular Please cite the article as: Zhang, Y., Miyauchi, M., & Nutt, S.. "Structure and properties of a phenylethynyl-terminated PMDA-type asymmetric polyimide," High Performance Polymers (2019), 31(3), 261-272, DOI: 10.1177/0954008318762592





weight generally yield reduced cross-link density in the cured polyimides, resulting in lower stiffness and greater toughness.³⁰ Indeed, the high molecular weight oligomer increased the tensile ductility and strength, although the elastic modulus of the cured polyimide was virtually identical to that of PMR-15 and AFR-PE-4. This peculiar behavior is attributed to the high backbone rigidity of TriA X. As discussed above, the pendent phenyl group raises the chain stiffness by hindering the rotation of diphenyl ether linkage, and in general, stiffer backbones exhibit greater elastic moduli.²⁵



Figure 9. Mechanical properties of TriA X (red), PMR-15 (blue) and AFR-PE-4 (yellow)*. *Only tensile properties at 23°C of AFR-PE-4 are displayed.

The high toughness observed can be attributed not only to the high molecular weight oligomer, but also the amorphous and loose-packed structure. The segmental chains between cross-link sites were randomly coiled together, resulting in high chain mobility upon stretching. Indeed, the





uncoiling of the polymer chains was responsible for the ductility observed at 232°C and 288°C. Beyond the yield points, polymer chains were able to slip over one other, producing the extended stress plateaus shown in Figure 7. If the polymer chains were straight rather than coiled, few intertwined segments would be stretched, and negligible plastic deformation would occur in tensile tests.

TriA X exhibited a tensile strength of 153.3 MPa and a strain-at-failure of nearly 10 %, even at -54°C. This behavior has important implications for polyimide composites, which are notoriously susceptible to cracking when cycled to low temperatures.⁴⁴ A polyimide matrix with superior low-temperature properties might resist microcracking upon exposure to cyclic temperature.

5 Conclusions

A materials paradigm was presented for an asymmetric polyimide system, demonstrating the effects of a pendent phenyl group on the polymer structure and properties at the molecular level. The key findings included: (1) the asymmetric/nonplanar backbone yielded amorphous structures with packing looser than VDW bonding in both imide oligomers and polyimides, independent of thermal history; (2) the disordered and loose molecular arrangement afforded more space for polymer chains to reconfigure above T_g , resulting in a low melt viscosity and hence improved processability; (3) the pendent phenyl group in the p-ODA moiety in the backbone hindered the rotation of diphenyl either linkage, leading to a $T_g = 362^{\circ}$ C; and (4) the high molecular weight oligomer and loose-packed amorphous structure of the TriA X polyimide resulted in high toughness, while the stiff backbone maintained an elastic modulus comparable to current polyimides (PMR-15 and AFR-PE-4). The materials paradigm presented here demonstrates an approach to eliminating crystallinity in polyimides without sacrificing other desirable properties. The results provide guidance for the design





and development of new high-performance polymers, especially for the scenarios of diminishing the crystallinity of semi-crystalline polymers.

The exceptional properties of the polyimide reported here have potential to expand the design space for high-temperature composites and thus lead to new applications for polyimide composites. The thermal and mechanical properties of the new polyimide surpassed those of conventional polyimides (PMR-15 and AFR-PE-4), which have been used effectively in high-temperature composite applications for decades. Composites fabricated from TriA X should open applications that require greater thermal stability or matrix-dominated mechanical properties than offered by present polyimides. Moreover, the unusual flexibility and toughness of TriA X may lead to high-performance applications for the neat polymer, including adhesives, coatings, and films.

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7 Declaration of Conflicting Interests

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