# Synthesis and Characterization of Poly(arylene ether sulfone)s with *trans*-1,4-Cyclohexylene Ring Containing Ester Linkages

# Bin Zhang, S. Richard Turner

Department of Chemistry, Macromolecules and Interfaces Institute (MII), Virginia Tech, Blacksburg, Virginia 24061 Correspondence to: S. R. Turner (E-mail: srturner@vt.edu)

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ABSTRACT: trans-1,4-Cyclohexylene ring containing acid chloride monomers were incorporated into poly(arylene ether sulfone) (PAES) backbones to study their effect on mechanical and thermal properties. The trans-1,4-cyclohexylene ring containing acid chloride monomers were synthesized and characterized by NMR and high-resolution mass spectrum. trans-1,4-Cyclohexylene containing PAESs were synthesized from the acid chloride monomers and hydroxyl terminated polysulfone oligomers with a pseudo-interfacial method and a solution method. These PAESs, with trans-1,4-cyclohexylene ring containing ester linkages, were fully characterized by NMR, thermogravimetric analysis, differential scanning calorimetry (DSC), size exclusion chromatography, and dynamic mechanical analysis (DMA). The tensile properties were also evaluated. The polymers made with the pseudo-interfacial method had relatively low molecular weights when compared to the solution method where much

**INTRODUCTION** Thermoplastic polyarylethers have been extensively studied since their initial discovery in the early 1960s.<sup>1</sup> Poly(arylene ether sulfone)s (PAESs), commonly known as polysulfones, are important commercial polymers with wide applications due to their excellent thermal and mechanical properties.<sup>2–5</sup> The literature contains many studies of PAES structures based on a variety of biphenols (BPs) and diphenylsulfones. The most common PAES structure is based on the reaction of bisphenol-A and 4,4'-dichloro-diphenylsulfone. This polymer is commercially sold as Udel<sup>®</sup> (Solvay Advanced Polymer LLC). However, some applications of PAES are limited by drawbacks such as poor resistance to some solvents, moderate impact resistance, and unacceptable thermal dimensional changes especially near  $T_g$  due to the PAES amorphous nature.<sup>1,6</sup>

An important structure modification for property improvement of polysulfone is to incorporate ester segments into the backbone. There are many reports of the synthesis of polysulfone polyester segmented copolymers for different applications with different synthetic methods.<sup>7–11</sup> In the work reported by McGrath and coworkers,<sup>12</sup> a glass-crystal higher molecular weight polymers were obtained. Crystallinity was promoted in the low molecular weight biphenol-based PAES samples with the pseudo-interfacial method. The crystallinity was confirmed by both the DSC and the wide angle X-ray diffraction results. The tensile test results of the high molecular weight polymers suggested that incorporation of the *trans*-1,4-cyclohexylene ring containing linkage slightly improved the ultimate elongations while maintaining the Young's moduli. The *trans*-1,4-cyclohexylene ring containing PAESs also showed higher sub- $T_g$  relaxations in DMA when compared with their terephthaloyl containing analog. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 4316–4324, 2011

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transition around 250 °C was observed with a narrow crystallization window about 30 °C in the BPs-based copolymer obtained by solution polymerization with terephthaloyl chloride (TC). Recently, Gaymans and coworkers<sup>13</sup> reported their synthesis of the bisphenol-A-based polysulfone polyester segmented copolymers by using the hydroxyl terminated PAES oligomer reacted with diphenyl terephthalate in melt or TC in solution. The reaction parameters, such as the reaction temperatures and the solvents, were systematically studied; no mechanical properties, however, were reported.

It is well known that the incorporation of *trans*-1,4-cyclohexylene rings into a polymer backbone can enhance the mechanical properties and affect the crystallization rate.<sup>14,15</sup> Poly(1,4-cyclohexylenedimethylene dimethylene terephthalate) (PCT) is an important commercial crystalline polyester and has a fast crystallization rate.<sup>14</sup> Increasing the trans/cis ratio of the cyclohexylene unit enhances the crystallization rate. Other 1,4-cyclohexylene ring containing polycarbonates and polyesters, such as poly(1,4-cyclohexylenedimethylene 1,4-cyclohexanedicarboxylate), and poly(butylene 1,4-cyclohexanedicarboxylate), have also been widely reported in the

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literature.<sup>16–21</sup> However, to the best of our knowledge, there are no report of *trans*-1,4-cyclohexylene ring containing PAESs.

In this article, we describe a systematic study on the effect of the incorporation of the trans-1,4-cyclohexylene ring containing polyester segments in the PAES backbones. Acid chloride chemistry which has been widely used in polyarylate and polyester synthesis.<sup>22,23</sup> A series of acid chlorides was designed and used as the trans-1,4-cyclohexylene ring containing segments to react with the PAES oligomers to yield the final PAESs with solution polymerization and pseudointerfacial polymerization.<sup>12</sup> In contrast to the interfacial polymerization technique where the reaction occurs at the interface, the reaction in pseudo-interfacial polymerization takes place in the organic phase and the side product is transferred into the aqueous phase with the assistance of the phase transfer agent. Two classes of oligomers, bisphenol-A and BP-based PAES oligomers, were chosen. The thermal and mechanical properties of the trans-1,4-cyclohexylene ring containing PAESs were evaluated by comparing with their terephthalic analogue and commercially available PAES Udel<sup>®</sup> and Radel<sup>®</sup> R provided by Solvay Advance Polymer. A complementary study on the molecular dynamics using solid-state NMR technique was also performed and described elsewhere.<sup>24</sup>

### **EXPERIMENTAL**

### **Materials**

All the chemicals were purchased from Aldrich with the exceptions of *trans*-1,4-cyclohexane dicarboxylic acid (CHDA) and *trans*-1,4-cyclohexane dimethanol (CHDM) which were provided by Eastman Chemical Company. The Udel<sup>®</sup> and Radel<sup>®</sup> R samples were provided by Solvay Advanced Polymers. Tetrahydrofuran (THF) was dried by PURE SOLV purification system from Innovative Technologies. Triethylamine (TEA), chloroform, *N*,*N*-dimethylacetamide (DMAc), and *N*-methyl-2-pyrrolidone (NMP) were treated with calcium hydride then purified by the vacuum distillation and stored over molecular sieves. All the other reagents were used as received without further purification.

### Instrumentation

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained by a JEOL 500 (500 MHz) spectrometer at room temperature with chemical shifts relative to tetramethylsilane (TMS). The FTIR data were obtained on an M2004 FTIR spectrometer from MIDAC Corporation from 400 to 650  $\text{cm}^{-1}$  with a resolution of 4  $cm^{-1}$ . The  $T_{gs}$  and  $T_{ms}$  were determined by differential scanning calorimetry (DSC). The data were obtained by using a TA Instruments  $^{\text{TM}}$  Q2000. Nitrogen was used as the carrier gas with a sample flow rate of 20 mL/min and a heating rate of 10 °C/min. The  $T_{g}$ s were determined in the second heating cycle after the samples were quenched at nominally 100 °C/min during the cooling cycle. The thermogravimetric analysis was carried out by a TA Instruments<sup>TM</sup> Q10 from 25 to 600 °C under nitrogen at a heating rate of 10 °C/min. The dynamic mechanical analysis (DMA) was performed on a TA Instruments<sup>™</sup> Q800 in nitrogen from −150 to 200 °C with



FIGURE 1 Structures of the acid chloride monomers.

a rate of 2 °C/min. The DMA parameters are Mode: Multi-Freq-Strain Tension film; Amplitude: 10  $\mu$ m; Preload force: 0.01 N. The tensile test was performed on an Instron Model 4400 Universal Testing System with a rate of 2 mm/min at room temperature. Size exclusion chromatography (SEC) was used to determine the molecular weights and the molecular weight distributions. The data were obtained in the SEC solvent at 30 °C on a Waters Alliance model 2690 chromatograph equipped with a Waters HR 0.5+ HR 2+ HR 3+ HR 4 styragel column set. Viscotek refractive index detector and a viscometer were used for the molecular weight determination. Polystyrene standards were utilized to construct a universal molecular weight calibration curve. Chloroform and NMP were used as the SEC solvents with a flow rate of 0.500 mL/min. The high-resolution mass spectrum (HRMS) was obtained from an Agilent LC/MS (liquid chromatography/mass spectrometry) mass spectrometer with a time of flight analyzer. The wide-angle X-ray diffraction was performed using a Rigaku S-Max 3000 3 pinhole SAXS/wide angle X-ray diffraction (WAXD) system. The X-ray source is the Cu Kα radiation, and the wavelength is 0.154 nm. Silver behenate is used to calibrate the sample-to-detector distance and the sample-to-detector distance is 82.5 mm. The WAXD two-dimensional images were obtained using an image plate, with an exposure time of 1 h and analyzed using the SAXSGUI software package.

### **Monomer Synthesis**

The structures and the abbreviations of the *trans*-1,4-cyclohexylene ring containing acid chloride monomers are shown in Figure 1. TC is commercially available and used as the aromatic analog.

### Synthesis of trans-1,4-Cyclohexanedicarbonyl Chloride

The glassware and the stir bar were predried in an oven at 80 °C for 12 h. To a 250-mL three-necked round-bottom flask equipped with a Teflon-coated magnetic stir bar, a condenser and an argon inlet, 16.00 g (93.02 mmol) of CHDA, 120.0 mL of thionyl chloride, and 0.1 mL of *N*,*N*-dimethylformamide (DMF) were added. The reaction was stirred in the presence of argon at 60 °C for 4 h. Then the excess amount of thionyl chloride was distilled out at 60 °C with vacuum. The white crystals were obtained and dried in vacuum oven





(-80 kPa) at room temperature for 12 h and then kept under argon atmosphere. The product was used directly in the next step without any further purification. Yield 94.4%. No melting point was observed due to instability.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$  2.73 (m, 2H),  $\delta$  2.30 (m, 4H),  $\delta$  1.58 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm):  $\delta$  188.4, 50.6, 30.0.

## Synthesis of trans-1,4-Cyclohexane-diylbis(methylene) bis(4-(chlorocarbonyl)benzoate)

About 10.00 g (49.26 mmol) of terephthaloyl chloride (TC) was dissolved in 80.0 mL dry THF in a three-necked roundbottom flask with a magnetic stir bar, an addition funnel and an argon inlet. A dry THF solution of 1.773 g (12.32 mmol) of *trans*-1,4-CHDM and 4.975 g (49.26 mmol ) TEA was added dropwise in a period of 1 h. The reaction mixture was stirred at room temperature for 12 h. Then excess water and TEA were added until a clear solution was obtained. After acidification, filtration was applied. The solid obtained was extracted with 600 mL of methanol twice and dried in a vacuum oven (-80 kPa) at 80 °C for 12 h. The white solid obtained after drying was identified as *trans*-1,4-cyclohexane-bis(methylene)bis(oxy)bis(oxomethylene) dibenzoic acid with a yield of 59.6%. No melting point was observed due to thermal decomposition below melting point.

<sup>1</sup>H NMR (DMSO- $d_6$ , ppm):  $\delta$  13.35 (s, 2H),  $\delta$  8.07 (s, 8H),  $\delta$ 4.15 (d, 4H),  $\delta$  1.85 (d, 4H),  $\delta$  1.75 (s, 2H),  $\delta$  1.13 (m, 4H). <sup>13</sup>C NMR (DMSO- $d_6$ , ppm),  $\delta$  167.2, 165.7, 135.5, 133.8, 130.2, 129.9, 70.2, 37.1, 28.8. HRMS (*m/z*) Calcd for C<sub>24</sub>H<sub>24</sub>O<sub>8</sub>: 440.1471; Found: 440.1469; Diff: 0.51 ppm.

The glassware and stir bar were predried in an oven at 80 °C for 12 h. To a 250-mL three-necked round-bottom flask equipped with a Teflon coated magnetic stir bar, a condenser and an argon inlet, 2.000 g *trans*-1,4-cyclohexane bis(methylene) bis(oxy) bis(oxomethylene)dibenzoic acid, 120.0 mL of thionyl chloride, and 0.1 mL of DMF were added. The reaction was stirred in the presence of argon at 60 °C for 4 h. Then the excess amount of thionyl chloride was distilled out at 60 °C with vacuum. The fresh product (*trans*-1,4-cyclohexane-diylbis(methylene) bis(4-(chlorocarbonyl)benzoate, TCT) was used directly in the next step without any further purification. A light yellow solid with a yield of 97.6% was obtained. No melting point was observed due to instability.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$  8.18 (m, 8H),  $\delta$  4.22 (d, 4H),  $\delta$  1.96 (d, 4H),  $\delta$  1.84 (s, 2H),  $\delta$  1.18 (m, 4H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, ppm),  $\delta$  168.0, 165.2, 136.7, 136.2, 131.3, 130.0, 70.5, 37.2, 29.0. HRMS (*m*/*z*) Calcd for C<sub>24</sub>H<sub>22</sub>O<sub>6</sub>Cl<sub>2</sub>: 476.0793; Found: 476.0762; Diff: -6.70 ppm.

### Synthesis of trans-1,4-Cyclohexane-diylbis(methylene) bis(4-(chlorocarbonyl)cyclohexanecarboxylate)

The compound *trans*-1,4-cyclohexane-diylbis(methylene) bis(4-(chlorocarbonyl)cyclohexanecarboxylate) (CCC) was synthesized in a similar way as compound TCT shown above. *trans*-Cyclohexane-1,4-diylbis(methylene))bis(oxy))bis(carbonyl))cyclohexane dicarboxylic acid was obtained as white powder with a yield of 50.9%. No melting point was observed due to thermal decomposition below melting point.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$  3.89 (d, 4H),  $\delta$  2.5– $\delta$  1.0 (m, 30H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm),  $\delta$  177.0, 175.3, 68.9, 42.3, 42.2, 37.2, 28.8, 28.2, 26.1. HRMS (*m/z*) Calcd for C<sub>24</sub>H<sub>36</sub>O<sub>8</sub>: 452.2410; Found: 452.2429; Diff 4.14 ppm.

CCC was obtained with a yield of 95.7% and used directly in the next step without any further purification. No melting point was observed due to instability.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$  3.84 (d, 4H),  $\delta$ 2.5– $\delta$  1.0 (m, 30H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm),  $\delta$  175.7, 175.2, 69.0, 51.9, 42.1, 37.2, 28.2, 28.1, 26.0. HRMS (*m/z*) Calcd for C<sub>24</sub>H<sub>34</sub>O<sub>6</sub>Cl<sub>2</sub>: 488.1732; Found: 488.1720; Diff: -2.52 ppm.

### **Polymer Synthesis**

### Synthesis of Hydroxyl-terminated PAES Oligomers with Controlled Molecular Weight

The reaction scheme is shown in Scheme 1. The hydroxylterminated bisphenol(bis-A) and the BP-based PAES oligomers with 2.0 kg/mol target molecular weight were synthesized by using the stoichiometry imbalance technique based on the Carothers equation. The bis-A-based PAES oligomer with 2.0 kg/mol target molecular weight is shown as an example. The BP-based oligomer was synthesized in a similar fashion. 5.036 g (17.54 mmol) of dichlorodiphenyl sulfone, 5.000 g (21.90 mmol) of bis-A, 7.870 g (56.95 mmol) of  $K_2CO_3,\ 80.0\ mL$  of DMAc, and 40.0 mL of toluene were added to a flask equipped with a mechanical stirrer, an argon inlet and a Dean-Stark trap. The reaction was heated to 140 °C for 3 h to remove water by azeotropic distillation. Then toluene was distilled out by increasing the temperature slowly to 160 °C in 2 h. After 20 h at 160 °C, the reaction mixture was cooled to room temperature. White solid was obtained by the precipitation of the reaction mixture in a 5 wt % of HCl aqueous solution and filtration. The product was thoroughly washed three times with 200-mL deionized water and methanol respectively. After drying at 120 °C for 12 h in vacuum oven (-80 kPa), the product was obtained with a yield of 92.4%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):  $\delta$  8.18 (m, 16.38),  $\delta$  7.21 (m),  $\delta$  7.06 (m),  $\delta$  6.96 (m),  $\delta$  6.91 (m),  $\delta$  6.72 (m, 4.00),  $\delta$  1.66 (m). In the proton NMR, the integration area ratio between the protons with the chemical shift of  $\delta$  6.72 and  $\delta$  8.18 was used to determine the number average molecular weights.

SCHEME 2 Synthesis of the trans-1,4-cyclohexylene ring containing PAES.

The actual molecular weights of the oligomers were very close to the target. For the bis-A PAES oligomer, the number average molecular weight was 2.0 kg/mol from the  $^{1}$ H NMR end group analysis.

# Synthesis of the High Molecular Weight Bis-A-Based and Biphenol-based PAESs

Bis-A-based and BP-based PAESs were both synthesized with comparable molecular weights to the Udel<sup>®</sup>, Radel<sup>®</sup> R samples and used as our lab-synthesized polymer controls in the thermal and the mechanical property evaluation. These high molecular weight samples were synthesized in the same way as the hydroxyl-terminated PAES oligomers shown above but with a different stoichiometry imbalance to control the molecular weights.

# Synthesis of the trans-1,4-Cyclohexylene Ring-Containing PAES

The *trans*-1,4-cyclohexylene ring containing PAES (Polymer 3 in Scheme 2) polymers were synthesized from the PAES oligomers and the diacid chloride monomers by pseudo-interfacial polymerization and solution polymerization.

### **Pseudo-Interfacial Polymerization**

Polymer

A typical polymerization for the copolymers is described below. 3.015 g (1.478 mmol) bis-A-based PAES oligomer was dissolved in 20.0 mL of chloroform in a two-necked roundbottom flask equipped with an argon inlet. Then a 5.0-mL aqueous solution of 1.020 g (7.389 mmol) K<sub>2</sub>CO<sub>3</sub> was added along with 0.038 g (0.150 mmol) tetraethylammonium iodide (TEAI) which worked as the phase transfer reagent. Under vigorous stirring, 0.300 g (1.478 mmol) terephthaloyl chloride in 20.0 mL chloroform was added. The reaction mixture was stirred at room temperature for 8 h. After precipitation in methanol and filtration, the polymer was washed three times with 100 mL water and 100 mL methanol, respectively. With a yield of 81.2%, the solid product was dried at 120 °C in a vacuum oven (-80 kPa) for 12 h.

### **Solution Polymerization**

High molecular weight materials were prepared with the solution method when dry chloroform or dry 1,1,2,2-tetrachloroethane was used as the solvent. A typical polymerization for the copolymers is described below. 3.015 g (1.478 mmol) bis-A-based PAES oligomer was dissolved in 20.0 mL of chloroform with addition of 0.373 g (3.695 mmol) TEA in a two-necked round bottom flask equipped with an argon inlet. Under vigorous stirring, 0.300 g (1.478 mmol) terephthaloyl chloride in 20.0 mL chloroform was added slowly in 1 h. A viscous solution was obtained after the reaction was performed at room temperature for another 8 h. After precipitation in methanol and filtration, the polymer was washed three times with 100 mL water and 100 mL methanol, respectively, to remove TEA hydrochlorides. With a yield of 91.9%, the solid product was dried at 120 °C in a vacuum oven (-80 kPa) for 12 h.

### **Polymer Film Preparation**

The film samples were obtained by the solution casting method. The solid polymer sample was dissolved at room temperature under stirring in chloroform, DMAc, or NMP depending on the results of solubility test to offer a homogeneous solution with concentration of 10% wt. After the filtration through a 45- $\mu$ m microglass fiber filter, the polymer solution was cast on a leveled glass substrate dried at 80 °C for 12 h and subsequently dried at 120 °C under vacuum (-80 kPa) for 12 h. The dog bone samples for the mechanical property evaluation were prepared from the polymer films. The dimension parameters of the dog bone sample were 4.00 mm in width and about 15 mm in length. The thickness of the samples was in the range of 60–100  $\mu$ m. The polymers offered transparent tough films with no color or light yellow color.

#### **RESULTS AND DISCUSSION**

# Solubility Results of the *trans*-1,4-Cyclohexylene Containing PAES

Solubility tests were performed at room temperature in chloroform, DMSO, DMAc, and NMP. The bis-phenol A-based polymers were readily dissolved in all the solvents listed. BPbased polymers showed low solubility in chloroform and DMSO and were soluble in DMAc and NMP. No solubility differences were found between the *trans*-1,4-cyclohexylene-





**SCHEME 3** Synthesis of the *trans*-1,4-cyclohexane bis(methylene) bis(4-(chlorocarbonyl)benzoate) (TCT).

containing and the 1,4-phenyl-containing polymers in the solvents studied.

### Synthesis of trans-1,4-Cyclohexylene Ring-Containing Diacid Chloride Monomers

Terephthaloyl chloride is commercially available and was used as the aromatic analogue. The 1,4-cyclohexanedicarbonyl chloride (CHDC) monomer (structure shown in Fig. 1) was obtained from the high conversion reaction of *trans*-CHDA with thionyl chloride.

In the synthesis of the new TCT and CCC trimer diacid chloride monomers, the corresponding diacid monomers were first synthesized by using an excess amount of terephthaloyl chloride (in case of TCT) or CHDC (in case of CCC). The synthesis scheme of TCT is shown in Scheme 3 as an example. After hydrolysis and acidification, the excess of terephthaloyl chloride ensured that only the trimer diacid monomer was formed in the first step with the terephthalic acid. The diacid monomer mixtures required a purification step to obtain the pure trimer diacid compound. This was accomplished by extraction twice with 600 mL methanol to remove the terephthalic acid. The obtained diacid monomer structures were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and HRMS. With the subsequent treatment of the trimer diacid with thionyl chloride, the desired trimer diacid chlorides TCT and CCC were obtained. This synthetic route was designed due to the difficulty to fully characterize the TCT and CCC diacid chloride monomers which are highly reactive. No melting points were observed for both the diacid monomers and diacid chloride monomers because they degrade below melting point.

### The Bis-A and BP-Based *trans-*1,4-Cyclohexylene Ring Containing PAES by Pseudo-Interfacial Polymerization

The bis-A and BP-based trans-1,4-cyclohexylene ring containing PAES polymers were synthesized from the PAES oligomers with 2.0 kg/mol target number average molecular weights and the diacid chloride monomer (structures shown in Fig. 1) at stoichiometry ratio. In pseudo-interfacial polymerization, the reaction took place in the organic phase and the side product HCl was transferred across the interface with the assistance of the phase transfer reagent TEAI. The polymer samples were characterized with FTIR. The appearance of the peak at 1,738 cm<sup>-1</sup> which is a characteristic peak of an ester carbonyl group showed up in the polysulfones containing ester linkages; while in the polysulfone oligomer samples, no peak was observed in this wavenumber range (shown in the supplemental material). This result combined with the disappearance of the hydroxyl characteristics IR peak at  $3,455 \text{ cm}^{-1}$  in the bis-A PAES with the ester segments confirmed the formation of the ester linkage and the successful polymerization. The molecular weight results shown later in this article also confirmed the successful polymerization. The samples were characterized by <sup>1</sup>H NMR in order to determine the trans-1,4-cyclohexylene ring conformation in the polymer backbone. A typical <sup>1</sup>H NMR spectrum of the trans-1,4-cyclohexylene ring containing PAES is shown in Figure 2 with the polymer structure. The enlarged area in the middle of Figure 2 shows the peak of the protons A which are the cyclohexyl protons next to the carbonyl groups. Only one signal (broadened by multiple splitting) was observed for proton A which indicated that no isomerization reaction occurred during the polymerization. Isomerization was not expected as the polymerizations were designed to be performed at low temperatures.

The molecular weights and the thermal properties of the pseudo-interfacial polymerization products were characterized (summarized in Table 1). All the polymer samples were dried in a vacuum oven thoroughly before characterization. Independent of polysulfone oligomer used, pseudo-interfacial polymerization yielded polymers with the number average molecular weights lower than 10 kg/mol. The polydispersity values of the polymers were all lower than the ideal value of 2.0. The low-polydispersity results from the loss of some low molecular weight fractions during the precipitation isolation procedure. In both bis-A PAES and BP PAES series, the terephthaloyl containing polymers (Bis-A\_TC and BP\_TC) had the highest glass transition temperatures. With the incorporation of the trans-1,4-cyclohexylene ring, the glass transition temperature decreased in the monomer sequence of CHDC > TCT > CCC. This  $T_g$  trend was as expected because the cyclohexylene ring incorporated in the polymer backbone can provide flexibility and facilitate the chain segment motion resulting in a decreased Tg. The bisphenol-A containing PAES polymers did not show melting transitions due to the tetrahedral isopropylidene units.



FIGURE 2 <sup>1</sup>H NMR spectrum of a typical *trans*-1,4-cyclohexylene ring containing PAES.

When the bis-A PAES oligomers were replaced by the BP PAES oligomers, crystallinity was found in all four polymer samples. Independent of the acid chloride monomers, the melting transitions of the polymers were all in the vicinity of 240 °C. The melting transition data of the BP\_TC sample is in close agreement with the reported value.<sup>12</sup> The DSC melting transition results were further confirmed by the WAXD measurements. All four BP-based PAESs showed similar WAXD pattern. An example pattern of BP\_TC is shown in Figure 3. Similar to the bis-A system, decreasing glass transition temperatures in the monomer sequence of TC > CHDC > TCT > CCC were found. Because of the structure independency of the melting transition, the decreasing glass transition temperatures enlarged the crystallization window defined as

**TABLE 1** Molecular Weights,  $T_{g}$ s and  $T_{m}$ s of the Bis-A and BPBased *trans*-1,4-Cyclohexylene Ring Containing PAES byPseudo-Interfacial Polymerization

	Molar Mass (kg/mol)					
Polymers	<i>M</i> <sub>n</sub>	$M_{\rm vv}$	PDI	$T_{g}$ (°C)	<i>T</i> <sub>m</sub> (°C)	$\Delta T$ (°C)
Bis-A_TC	11.5	22.7	1.9	182	-	-
Bis-A_CHDC	10.5	16.3	1.5	168	-	-
Bis-A_TCT	6.9	10.9	1.6	160	-	-
Bis-A_CCC	10.8	17.4	1.6	155	_	-
BP_TC	6.2	9.2	1.5	200	247	47
BP_CHDC	5.2	8.4	1.6	186	244	48
BP_TCT	3.6	7.7	2.1	177	241	64
BP CCC	4.2	5.6	1.3	167	244	77

the temperature difference between  $T_{\rm g}$  and  $T_{\rm m}$  (shown as  $\Delta T$  in Table 1). The DSC curve of samples BP\_CCC is shown in Figure 4 with a crystallization window of 77 °C. In the DSC study, the samples were quenched at nominally 100 °C/min or cooled at a rate of 2 °C/min in the cooling cycles. It needs to be noted that independent of the cooling rate, neither recrystallization nor melting transition were observed in the cooling cycle and the second heating cycle of the DSC curves in all the polymers. These results indicated that the semicrystallinity was a result of the solvent-induced crystallization with relatively low molecular weight samples. A slow crystallization



FIGURE 3 Small-angle X-ray diffraction pattern of the BP\_TC sample.





**FIGURE 4** DSC curves of the BP based *trans*-1,4-cyclohexylene ring containing PAES synthesized from CCC(BP\_CCC sample).

### The Bis-A and BP-Based *trans*-1,4-Cyclohexylene Ring Containing PAES by Solution Polymerization

Attempts to cast films from the *trans*-1,4-cyclohexylene ring containing polymers prepared by pseudo-interfacial polymerization resulted in brittle films due to the low molecular weights. In order to obtain high quality films for the mechanical property characterizations, *trans*-1,4-cyclohexylene ring containing PAESs were prepared from solution by using the same starting materials at stoichiometry ratio. For the bisphenol-A series, chloroform was chosen, because it is easy to dehydrate and the oligomer and the product are both soluble. Chloroform was not used for the BP series, because the solubility of the starting oligomer is very low to provide a high concentration for the solution polymerization. Furthermore, the solubility of the polymer product is limited. Different solvent systems including DMAc, DMF, NMP, and

**TABLE 2** Molecular Weights,  $T_gs$ , and  $T_ms$  of the Bis-A and BP Based *trans*-1,4-Cyclohexylene Ring Containing PAES by Solution Polymerization with Controls

	Molar Mass (kg/mol)					
Polymers	<i>M</i> <sub>n</sub>	$M_{\rm vv}$	PDI	$T_{g}$ (°C)	<i>T</i> <sub>m</sub> (°C)	T <sub>d</sub> <sup>a</sup> (°C)
Udel <sup>®</sup>	22.8	41.7	1.8	189	-	498
BisA PAES	20.8	36.0	1.7	186	_	537
Bis-A_TC	24.6	49.9	2.0	189	_	480
Bis-A_CHDC	23.2	36.1	1.5	181	_	466
Bis-A_TCT	11.0	28.7	2.6	163	_	429
Bis-A_CCC	9.6	18.4	1.9	159	_	450
Radel <sup>®</sup> R	14.2	28.8	2	220	_	526
BP PAES	21.6	37.4	1.7	227	_	565
BP_TC	10.8	32.5	3.0	220	_	541
BP_CHDC	9.3	24.7	2.6	211	_	497
BP_TCT	8.6	17.8	2.1	196	_	448
BP_CCC	10.5	28.9	2.7	185	_	469

<sup>a</sup> 5 % weight loss temperature in nitrogen.

DMAc/Chloroform were used. In agreement with a previous report,<sup>13</sup> in our system, the solvents listed above resulted in low molecular weight products probably due to a small amount of water which hydrolyzed some of the diacid chloride and disrupted the stoichiometry balance. Successful solution polymerization was obtained in 1,1,2,2-tetrachloroethane which provided good solubility to the starting materials and the products. The polymer products from solution were also characterized by FTIR and <sup>1</sup>H NMR. The results were similar to the results from the polymers by pseudo-interfacial polymerization as shown earlier. The successful polymerization was confirmed by the appearance of the ester carbonyl peak in the FTIR of the products. The trans-1,4-cyclohexylene ring conformation was confirmed by the <sup>1</sup>H NMR peak of the cyclohexyl protons next to the carbonyl groups.

The molecular weights and thermal properties of the polymer products with solution polymerization are summarized in Table 2. For both of the bis-A- and BP-based PAES, the solution method yielded polymers with higher molecular weights than those from the pseudo-interfacial polymerization. The molecular weights of cyclohexylene ring containing polymers were comparable to the molecular weight of the Udel<sup>®</sup> and Radel<sup>®</sup> R controls so that the mechanical properties of those polymers were evaluated without having molecular weight as a factor. The SEC traces of the polymers from the solution method were all observed with monomodal peaks with no sign of branching or crosslinking. No crystallinity was found in the BP-based PAES samples listed in Table 2. As the repeat unit structures are the same for the samples with the pseudo-interfacial and solution polymerization, the loss of crystallinity could be due to the combination of higher molecular weights and slightly larger PDIs (Polydispersity Index) with the solution method compared to those with the pseudo-interfacial methods. The fact that

**TABLE 3** Tensile Test Results of the Bis-A and BP Based *trans*-1,4-Cyclohexylene Ring Containing PAES by SolutionPolymerization with Controls

Polymers	Modulus (MPa)	Strain at Failure (%)
Udel <sup>®</sup> control	$1304\pm86$	$6.4\pm0.5$
Bis-A PAES	N/A <sup>a</sup>	N/A
Bis-A_TC	$1550\pm106$	$15.4\pm3.9$
Bis-A_CHDC	$1504\pm108$	$13.9\pm3.6$
Bis-A_TCT	$1318\pm73$	$17.5\pm8.6$
Bis-A_CCC	$1417\pm169$	$14.4\pm2.4$
Radel <sup>®</sup> R control	$1353\pm92$	$8.1\pm1.3$
BP PAES	$1498\pm140$	$7.9\pm0.8$
BP_TC	1758 ± 137	$8.4\pm0.8$
BP_CHDC	$1175\pm92$	$34.9\pm11$
BP_TCT	$1216\pm100$	$8.2\pm1.2$
BP_CCC	1329 ± 315	9.9 ± 1.5

 $^{\rm a}$  N/A, not available, the sample resulted in brittle film in solution casting.



**FIGURE 5** DMA curves of the bis-A-based *trans*-1,4-cyclohexy-lene ring containing PAES and its aromatic analogue.

higher molecular weight results in lower crystallinity has been reported in polymer such as polyethylene and polyetheretherketone.<sup>25–27</sup> Similar to the results in the pseudo-interfacial polymerization, in both series, the terephthaloyl containing polymers had the highest glass transition temperatures and the glass transition temperature decreased in the sequence of TC > CHDC > TCT > CCC as expected.

The bis-A-based and BP-based PAESs were both synthesized with comparable high molecular weights to the Udel<sup>®</sup>, Radel<sup>®</sup> R samples and used as our lab-synthesized polymer controls in mechanical property evaluation. The film tensile test results, summarized in Table 3, suggested that the *trans*-1,4-cyclohexylene ring containing PAES exhibited approximately the same Young's moduli as their aromatic analogue and the property controls. Moderate ultimate elongation improvements were observed in the *trans*-1,4-cyclohexylene ring containing polymers. This result is in agreement with a similar moderate elongation enhancement in *trans*-1,4-cyclohexylene containing polyketone polysulfone previously published.<sup>28</sup>

In the DMA tests, the trans-1,4-cyclohexylene ring containing PAES showed a higher relaxation, with the peak temperature value in the vicinity of -70 °C, than their aromatic analog. Typical DMA curves of the *trans*-1,4-cyclohexylene containing PAES and the terephthaloyl containing PAES are shown in Figure 5. The enlarged area is the DMA low temperature region. At the peak value in the vicinity of -60 °C, the *trans*-1,4-cyclohexylene ring containing PAES showed a large lowtemperature relaxation which was absent in the aromatic analogue. The observed sub- $T_{\rm g}$  relaxation has been well reported in the literature. Similar relaxations were observed in a series of 1,4-cyclohexylene ring containing polyesters with a peak value at around -55 °C.<sup>17</sup> In the secondary relaxation study reported by Chen and Yee,<sup>15</sup> a low-temperature relaxation with the peak value about -75 °C was observed in PCT. On the basis of the references, we propose that the origin of the secondary relaxations in our PAESs samples is the conformation transition of the backbone trans-1,4-cyclohexylene ring.<sup>29</sup> This enhanced low-temperaARTICLE

ture relaxation suggested that the incorporation of the *trans*-1,4-cyclohexylene ring can potentially enhance the impact strength without sacrificing modulus.

### CONCLUSIONS

The incorporation of the trans-1,4-cyclohexylene rings into a polymer backbone is well known to have a dramatic influence on the polymer properties such as crystallinity, thermal, and mechanical properties. In this article, trans-1,4-cyclohexylene ring units were successfully introduced into the PAES backbones by the reactions of a series of diacid chloride monomers and the hydroxyl-terminated PAES oligomers. Crystallinity was achieved in the BP-based trans-1,4-cyclohexylene ring containing PAESs with the pseudo-interfacial method but not in the bisphenol-A-based polymers. Recrystallization was not observed in the second heating cycle of the DSC measurement likely due to the slow crystallization rate of the copolymer in the melt state. The mechanical properties of the high molecular weight trans-1,4-cyclohexylene ring polymers from the solution polymerization were evaluated. Both the tensile properties and the DMA results suggested that the incorporation of trans-1,4-cyclohexylene ring ester linkages improves the ultimate elongation and promotes sub-Tg relaxations while maintaining the moduli of the polymers.

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