Design and Synthesis of Thermal Contracting Polymer with Unique Eight-Membered Carbocycle Unit

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*Supporting Information

ABSTRACT: It is uncommon for a solid substance to expand upon cooling and contract upon heating. In this work, we synthesized a carbocycle monomer that contains 1,2:5,6-dibenzocyclooctadiene (DBCOD) unit and the corresponding polymers with different amounts of DBCOD in the polymer main chain. The films produced from this DBCOD-based polymer showed reversible thermal contraction behavior with the negative thermal expansion (NTE) coefficient of −625 ppm/K (100–200 °C). Differential scanning calorimetry (DSC), variable-temperature nuclear magnetic resonance (VT-NMR), and density-functional theory (DFT) calculations indicated that the population of the chair conformer of DBCODs increased with the rise of temperature due to the conversion from twist-boat to chair conformer. This led to giant thermal contraction. Furthermore, the value of the NTE coefficient could be adjusted by the amount of DBCODs and their surrounding physical environment. This is the first demonstration of a linear polymer that exhibits reversible thermal contraction. The new monomer can be covalently incorporated into a variety of polymeric materials to construct negative thermal expansion or zero expansion materials for the specific applications.

INTRODUCTION

Solid materials typically show thermal expansion due to the increasing anharmonicity vibrational amplitudes of atoms, ions, or molecules. The increased macroscale dimension of materials accompanying temperature increase could cause cracking, fatigue, or delamination, leading to deterioration and ultimately device failure.1 To reduce thermal expansion, burgeoning efforts have been made recently on developing materials that exhibit negative thermal expansion (NTE), i.e., shrinking upon heating.2,3 The majority of NTE materials are inorganics such as metal oxides and zeolites.4,5 These materials have used to suppress coefficient of thermal expansion (CTE) by forming composites, e.g., ZrW2O8 and GaNMn3/epoxy composites,6−9 and Zr3WP2O12 and ZrW2O8/polyimide composites,10,11 which will provide potential applications ranging from fiber-optics coating, electronic packing, and tooth filling to aerospace.2 However, most of the systems possess weak interface connectivity between NTE components and their surrounding matrix materials. Moreover, they do not offer desirable CTE at a suitable temperature window for practical applications.12,13 Organic materials such as organic frameworks,14−16 organic crystals,17 and liquid-crystalline materials18 offer significantly higher NTE values than inorganic NTE materials. However, they are often chemically and thermally unstable. One direction of thermal contraction is usually accompanied by thermal expansion of other direction(s).19,20 Hence, a system that offers tunable and large NTE at the device operation temperature and simultaneously offers excellent processing capability for incorporation into a device is of particular importance.

Through a long-term investigation, we revealed the first example of NTE polymer in 2013, which was prepared by high-temperature cross-linking (350 °C) of benzocyclobutene (BCB)-containing polyarylamide.21 This polymer showed large negative thermal expansion. The NTE value was 6 times higher than any known systems under similar operating conditions.14,17,22,23 Further exploration showed that the NTE effect stemmed from an unique structure, that is, BCB dimer-1,2:5,6-dibenzocyclooctadiene (DBCOD). Theoretical calcu-
lations and experimental investigations demonstrated that the enthalpy-driven conformational transition of BDCOD from twist-boat (TB) to chair (C) is the original of the thermal contraction. More recently, we found that submolecular substitution can be used to introduce molecular asymmetry that can facilitate the BDCOD conformational conversion, leading to larger negative thermal expansion.24,25 However, there are several issues related to these systems, such as (i) uncertain amount of BDCOD units due to great numbers of side reactions accompanying BCB dimerization,26 (ii) sluggish BDCOD conformational transition as BDCODs are located in the cross-linking positions, and (iii) the dimerization temperature is close to the polymer degradation temperature.

While the synthesis of eight-membered carbocycles is a long-term challenge to organic chemists,29 the dimerization of benzocyclobutene as we used previously easily produces byproducts and low reaction yield.26 To address the aforementioned limitations, in this work, we prepared BDCOD-containing functional monomer and corresponding polyarylamides where BDCODs are located in the main chain. It could offer some distinguishing advantages, such as (1) the amount of BDCODs is known and can be adjusted, (2) BDCODs are not in the cross-linking positions and thus the polymers can be readily processed such as aligning all BDCODs for even greater thermal contraction in a specific direction, and (3) the polymer also can be reworked. Hence, we first employed a new synthetic route to prepare dicarboxyl-substituted BDCOD functional monomer and synthesized a series of polyarylamide with varied BDCOD content using Yamazaki–Higashi phosphorylation polycondensation. The molecular structures of as-synthesized polymers were further characterized by means of nuclear magnetic resonance (NMR), Fourier transform-infrared spectroscopy (FT-IR), and gel permeation chromatography (GPC). Their thermal properties, optical properties and mechanical properties were evaluated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), UV−vis−NIR spectograph, and mechanical testing instrument. Then, the thermal expansion/contraction behaviors of the solution-casted polymer films were tested directly by thermomechanical analyzer (TMA), which showed substantial thermal contraction over a wide range of temperatures, with the observed optimal CTE value of −625 ppm/K (100−200 °C). Furthermore, DSC, variable-temperature nuclear magnetic resonance (VT-NMR), and density-functional theory (DFT) calculations were employed to reveal the driving force of unique thermal contracting behaviors.

*Experimental Section*

**Materials.** 3,4’-Oxydianiline (ODA, 97%), 4,4’-oxydibenzoic acid (ODA, 98%), and N-methyl-2-pyrrolidone (NMP, anhydrous) were supplied by J&K and used as received. All other reagents were purchased from commercial chemical suppliers and used without further purification.

**Synthetic Procedures of BDCOD Monomer.** *5-Methylene-10,11-dihydro-5H-dibenzo[a,d]l[7]annulene* (Compound 1). Methyltriphenylphosphonium iodide (21.0 g, 52 mmol) was added to an oven-dried 250 mL Schlenk tube. After deoxygenated by freeze−pump−thawing with N2 for three times, anhydrous THF (40 mL) was added via syringe, creating a milky white suspension. At 20 °C, KOBu (5.83 g, 52 mmol) was added as a solid to the stirring suspension, generating bright yellow methylenetriphenylphosphorane ylide. After allowing the mixture to stir for 20 min, dibenzosuberone (8.33 g, 40.0 mmol) was added via syringe slowly, yielding crimson suspension. The reaction was stirred at 40 °C for another 12 h and filtrated through a plug of silica gel with dichloromethane (DCM) as eluent to remove unreacted ylide/base. The concentrated compound was further purified via silica gel column chromatography (1:10 DCM:Hex) to yield 7.67 g (93%) of white powder (1). *1H NMR (400 MHz, acetone-d$_6$) δ 7.34 (d, _J_ = 7.0 Hz, 2H), 7.25−7.11 (m, 6H), 5.40 (s, 2H), 3.11 (s, 4H) (Figure S1). *13C NMR (101 MHz, acetone-d$_6$) δ 152.44, 141.26, 138.51, 128.15, 127.99, 126.43, 116.91, 33.24 (Figure S2). MS (ESI) m/z for C$_{16}$H$_{14}$O$_2$ [M − H]$^+$ calculated: 205.1, found: 205.2.*

11,12-Dihydrodibenzo[a,e][8]annulene-5(6H)-one (Compound 2). Compound 1 (6.18 g, 30 mmol) was added in 95% methanol (150 mL). After being stirred at 40 °C for nearly 30 min, the solid was dissolved to give a colorless solution. Then, crystalline [hydroxy-(tosyloxy)iodo]benzene (HTIB) (10.7 g, 27.0 mmol) was added and stirred at room temperature for 2 h, and the solvent was removed in vacuo to give an oil mixture. The mixture was partitioned between DCM (50 mL) and H$_2$O (50 mL) and transferred to a separatory funnel. The organic layer was separated, washed with H$_2$O (50 mL × 2) and brine (50 mL × 2), dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo to give a bright yellow oil, which was subjected to flash column chromatography on silica gel (1:6 DCM:Hex) to give 5.28 g (88%) white powder (2). *1H NMR (400 MHz, acetone-d$_6$) δ 7.39−6.95 (m, 6H), 4.18 (s, 2H), 3.34 (qd, _J_ = 8.8, 2.2 Hz, 4H) (Figure S3). *13C NMR (101 MHz, acetone-d$_6$) δ 203.43, 139.30, 139.16, 138.60, 134.43, 131.60, 131.12, 130.64, 130.11, 127.97, 127.46, 126.70, 126.63, 51.31, 34.68, 33.42 (Figure S4). MS (ESI) m/z for C$_{16}$H$_{14}$O$_2$ [M − H]$^+$ calculated: 222.1, found: 222.2.*

5,6,11,12-Tetrahydrodibenzo[a,e][8]annulene (Compound 3). Dry diethyl ether (200 mL) was added in a 500 mL, three-necked round-bottom flask equipped with a condenser and addition N$_2$ pipe and placed in an ice bath. Then, AlCl$_3$ (17.25 g, 130.0 mmol) and LiAlH$_4$ (2.46 g, 65.0 mmol) were added slowly in turn to the ether solution and kept stirring for 20 min. A solution of compound 2 (4.80 g, 21.6 mmol) in ether (20 mL) was then added dropwise. After stirring for 1 h, ethyl acetate (10 mL) was added dropwise to decompose excess reagent. The mixture was poured into cold saturated NH$_4$Cl solution (200 mL), and the organic layer was separated and washed with saturated brine solution (100 mL). The aqueous layer was further extrated with DCM (100 mL × 2), and the extracts were combined with the ether solution and dried over anhydrous Na$_2$SO$_4$. After evaporating, the yellow crude product was recrystallized from hexane to yield 4.05 g (90%) of white crystals (3). *1H NMR (400 MHz, CDCl$_3$) δ 7.13−6.99 (m, 6H), 3.13 (s, 8H) (Figure S5). *13C NMR (101 MHz, CDCl$_3$) δ 140.89, 129.97, 126.41, 35.45 (Figure S6). MS (ESI) m/z for C$_{16}$H$_{16}$O$_2$ [M − H]$^+$ calculated: 208.1, found: 208.1.*

5,6,11,12-Tetrahydrodibenzo[a,e][8]annulene-2,9-dicarbalddehyde (Hyde Compound). Compound 3 (4.17 g, 20 mmol) was added to an oven-dried 250 mL Schlenk tube with 60 mL of dry DCM held at −10 °C. After purging the vessel with N$_2$, stannic chloride (20.8 g, 80 mmol) and dichloromethyl methyl ether (9.2 g, 80 mmol) were added dropwise to the mixture in turn. After the mixture stirred at −10 °C for 4 h, it was allowed to warm to room temperature and stirred for an additional 2 days. The mixture was poured into saturated NaHCO$_3$ solution (200 mL) and stirred for 1−2 h until the organic layer turned slight yellow. The DCM extract was washed with water, dried, and concentrated to give a pale yellow solid. The crude product was purified by column chromatography over silica gel (1:8 EtOAc:Hex) to yield 3.07 g (58%) of the mixture of methylnethedicarbalddehyde-substituted dibenzydicoclaotadene isomers. The isomer mixture was further purified by column chromatography over silica gel carefully using 1:2 mixture of DCM:Hex as eluent. The first fraction of eluent gave 0.85 g (16%) of 5,6,11,12-tetrahydrodibenzo[a,e][8]annulene-2,9-dicarbalddehyde as a white powder. *1H NMR (400 MHz, CDCl$_3$) δ 9.83 (s, 2H), 7.48 (d, _J_ = 8.9 Hz, 4H), 7.12 (d, _J_ = 7.6 Hz, 4H), 3.21 (s, 8H) (Figure S7). The second fraction of eluent gave 2.22 g (42%) of target compound 4 as white powder. *1H NMR (400 MHz, CDCl$_3$) δ 9.83 (s, 2H), 7.48 (d, _J_ = 4.6 Hz, 4H), 7.12 (d, _J_ = 7.6 Hz, 2H), 3.22 (d, _J_ = 4.1 Hz, 8H) (Figure S8). *13C NMR (101 MHz, CDCl$_3$) δ 192.32, 147.38, 141.57, 135.06, 135.00, 131.10, 130.80, 130.67, 126.70, 126.63, 51.31, 34.68, 33.42 (Figure S4).
A typical mmol), NaH2PO4 (2.34 g, 15 mmol), and NaClO2 (2.71 g, 30 mmol) was added dropwise in 30 min to a stirred mixture of compound 7.50 (d, 6J = 12.7 Hz, 4H), 7.03 (d, 6J = 7.7 Hz, 2H), 3.12 (s, 8H) (Figure S10). 13C NMR (101 MHz, DMSO-δ6) 167.93, 145.82, 145.72, 140.62, 131.23, 131.17, 130.62, 130.56, 129.16, 129.12, 127.88, 127.86, 127.84, 126.34, 126.24, 124.16, 134.00 (Figure S11). MS (ESI) m/z for C18H16O4 [M+H]+ calculated: 284.1, found: 284.1. 13C NMR (101 MHz, DMSO-δ6) δ 167.93, 145.82, 145.72, 140.62, 131.23, 131.17, 130.62, 130.56, 129.16, 129.12, 127.88, 127.86, 127.84, 126.34, 126.24, 124.16, 134.00 (Figure S11). MS (ESI) m/z for C18H16O4 [M+H]+ calculated: 295.1, found: 295.1.

Preparation of DBCOD-Containing Functional Polyarylamides. The Yamazaki–Higashi phosphorylation polycondensation technique was used to prepare the polyarylamides. A typical example for the preparation of DBODA1 is given to illustrate the procedure. 30,31 The precursor polymer was prepared by an analogous procedure. The crude product was further dissolved in LiOH aqueous solution and washed by EtOAc (50 mL x 3) to remove starting material and intermediates. Then, the solution was acidified with aqueous HCl to pH 3 again, centrifugation, and washed by water; repeat this procedure for twice to get 0.64 g (72%) of white powder. 3H NMR (400 MHz, DMSO-δ6) δ 12.73 (s, 2H), 7.50 (d, 6J = 12.7 Hz, 4H), 7.03 (d, 6J = 7.7 Hz, 2H), 3.12 (s, 8H) (Figure S10). 13C NMR (101 MHz, DMSO-δ6) δ 167.93, 145.82, 145.72, 140.62, 131.23, 131.17, 130.62, 130.56, 129.16, 129.12, 127.88, 127.86, 127.84, 126.34, 126.24, 124.16, 134.00 (Figure S11). MS (ESI) m/z for C18H16O4 [M+H]+ calculated: 295.1, found: 295.1.

**Preparation of DBCOD-Containing Functional Polyarylamides.** The Yamazaki–Higashi phosphorylation polycondensation technique was used to prepare the polyarylamides. A typical example for the preparation of DBODA1 is given to illustrate the procedure. A 25 mL Schlenk tube equipped with a magnetic stirrer was charged with 148.2 mg (0.5 mmol) of DBCOD, 258.2 mg (1.0 mmol) of OBA, 500.3 mg (1.5 mmol) of ODA, 1.0 mL of triphenyl phosphite (TPP), 3.0 mL of anhydrous NMP, 0.6 mL of pyridine, and 300.0 mg of calcium chloride (CaCl2). The reaction mixture was degazoygenated by freeze–pump–thawing for three times and then immersed into an oil bath thermostated at 120 °C for 10 h. After the polymer solution cooled to room temperature, the resulting solution was poured slowly into 200 mL of stirring methanol. The fiber-like precipitate was filtered off, washed thoroughly with methanol and hot water, and dried under vacuum. The other polyarylamides were prepared by an analogous procedure.

**Formation and Characterization of Polymer Films.** Silicon substrates were cleaned by treatment with a freshly prepared piranha solution (1:3 v/v mixture of 30% H2O2 and 98% H2SO4) at 90–100 °C for 1 h, rinsed with deionized water, and dried in an oven. The fully dissolved polymer solution (60 mg/mL in NMP) was poured on a clean silicon substrate. After drying at 50 °C for 3 days, the films were annealed at 120 °C under vacuum for another 12 h and then peeled off from the substrates with the help of a knife. The obtained films were about 40–80 μm in thickness and were used for FT-IR, XRD, UV–vis–NIR, and thermal mechanical analysis.

**Mechanical Properties Investigation.** The mechanical properties of the polyarylamide films were tested with an Instron 5565 mechanical testing instrument with a load cell of 500 N at room temperature. The gauge length is 30 mm, and the cross-head speed is 15 mm min−1. Three replicates from the individual films were tested, and average values were used as final results.

**Thermal Expansion/Contraction Behavior of Polymer Films.** Thermal expansion/contraction behavior of polymer films were analyzed by a Mettler Toledo-SDT A884 e thermomechanical analyzer (TMA). Polymer film was cut into a uniform 15 mm x 3 mm (effective length 10 mm) film, the tensile load was 5 mN, and nitrogen flow rate was 40 mL/min. The linear thermal expansion coefficient of a material at constant pressure can be calculated according to eq 1:

\[
\alpha = \frac{1}{L_0} \frac{\Delta L}{\Delta T}
\]

where \(\Delta L/\Delta T\) is the change rate of the sample length with temperature and \(L_0\) is the initial sample length. For reversible thermal contraction detection, samples were measured with the heating rate of 5 °C/min for several times after reset at 40 °C for 8, 10, 15, 17, 24, and 42 h after the last measurement. The recovery ratio is defined as the ratio of the contraction value at a given interval of time to the initial contraction value ratio.

**Variable-Temperature NMR.** Variable-temperature NMR spectroscopy was carried out on a Bruker Avance III spectrometer with liquid nitrogen transfer line operating at 600 MHz and varied temperatures (−108 to 25 °C) for H using CDCl3 (with 20% CS2) solvents and tetramethylsilane (TMS) as a reference. The sample concentration is 2 mg/mL. Scan number for H NMR measurements is 64. Data were reported as follows: chemical shift (δ) measured in ppm downfield from TMS.

**Conformational Change Characterized by DSC.** DSC was used to detect thermally induced molecular conformational change. The preannealed polymers (3–5 mg) encapsulated in an aluminum pan were heated from −50 to 130 °C at a heating rate of 2 °C/min with the nitrogen flow rate of 50 mL/min. The samples were measured with the same procedures for several times after resetting at 40 °C in a DSC oven for 0, 4, 8, and 24 h.

**Computational Details.** All the calculations were performed with the wb97XD density functional method using the Gaussian 09 software package. The 6-31+G(d,p) basis set was used. Harmonic vibrational frequency analyses were carried out to confirm if the optimized structure is a genuine energy minimum or a transition state.

**Instrumentation and Measurements.** 1H NMR and 13C NMR spectra were recorded at ambient temperature on a Bruker Avance-400 FT-NMR spectrometer, operated at 400.0 MHz for the proton nuclei. ESI-MS were routinely measured on a Varian SATURN 2000 instrument. Routine FT-IR spectra were measured at room temperature on a Nexus 470 spectrometer (Thermo Fisher, US) with 32
scans, spanning a spectral range of 4000−500 cm⁻¹ with a resolution of 4.0 cm⁻¹. Samples were prepared by pressing dry potassium bromide (KBr) and the polymer mixture before the measurement. Molecular weights (Mn, Mw) and polydispersity (Mw/Mn) of the synthesized polymer samples were measured at 55 °C on an Agilent 1260 gel permeation chromatograph (GPC) equipped with refractive index detector (RI). Dimethylformamide (DMF) was utilized as the eluent at a flow rate of 1.0 mL/min, and a series of commercial poly(methyl methacrylate) (PMMA) standards were employed to calibrate the GPC elution traces. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pyris 1 TGA instrument. Experiments were carried out on approximately 3 mg of samples heated in flowing nitrogen (flow rate = 50 mL/min) at a heating rate of 20 °C/min. Thermal transition behaviors were measured using a TA Q2000 DSC instrument. Samples (5−8 mg) encapsulated in an aluminum pan were first heated to 350 °C, thermostated for 5 min to eliminate the thermal history, cooled to −50 °C, and then heated to 320 °C at a rate of 10 °C/min with the nitrogen flow rate of 50 mL/min. The glass transition temperature (Tg) was measured as the midpoint of the heat capacity jump from the second heating scan. UV−vis−NIR spectrometer measurements (Lambda 750, PerkinElmer) were carried out to characterize the light absorption of the films, with the spectra range of 400−1200 cm⁻¹. Wide-angle X-ray diffraction (WAXD) was carried out by a Rigaku X-ray diffractometer with a Ni-filtered Cu Kα radiation (λ = 0.154 nm) at room temperature. The scan rate was 5°/min from S° to 40°. The selected voltage and current were 40 kV and 200 mA, respectively. The morphology of the polymer films were analyzed by an atomic force microscope (AFM) on a Multimode 8 (Brucker, US), taken in the tapping mode.

**RESULTS AND DISCUSSION**

**Preparation and Characterization of Series of DBCOD-Containing Polyarylamides.** First, the DBCOD unit 3 and the corresponding dicarboxylic acid monomer 5 were synthesized according to the pathways shown in Figure 1.

![Figure 2. 1H NMR (a) and FT-IR spectra (b) for the prepared DBODA copolymers.](image)

![Table 1. Summarized Data for the Prepared Polyarylamide Copolymer Series](table)

<table>
<thead>
<tr>
<th>sample</th>
<th>monomer feeding ratio</th>
<th>x:y:z</th>
<th>DBCOD content (wt %)</th>
<th>M_c (kg mol⁻¹)</th>
<th>M_w (kg mol⁻¹)</th>
<th>M_w/M_c</th>
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<td>13.4</td>
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<td>33.6</td>
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</table>

*Représent feeding molar ratios of monomers OBA:DBCOD-COOH:ODA. ²x:y was calculated by ¹H NMR with the integration of the peak signals at δ10.07 and 10.27 ppm (Figure 2a). ³DBCOD content were determined by the weight ratio of DBCOD unit to the whole polymer chain. Data mean weight-average molar mass (M_w), number-average molar mass (M_n), and polydispersity index (M_w/M_n) determined by GPC with DMF as eluent (1 mL/min) calibrated by the PMMA standard.

Starting from commercial dibenzosuberone, the Wittig−HTIB ring expansion reaction⁵⁸,⁵⁹ was carried out to generate eight-membered cyclooctanone 2 in good yield (82%), and standard reduction conditions⁶⁰ by LiAlH₄−AlCl₃ were applied to generate DBCOD 3. Formylation⁶¹ of 3 via the Rieche reaction gave two products, 2,8-dicarbaldehyde-substituted DBCOD and 2,9-dicarbaldehyde-substituted-DBCOD 4, with the isolated yield of 16% and 42%, respectively. The major component 4 was subsequently transformed to target compound 5 via a standard Pinnick oxidation reaction⁶² converting aldehyde to carboxyl groups. The combined yield of five step organic transformations for the product of DBCOD-COOH is 22%. ¹H NMR and ¹³C NMR spectra are shown in the Supporting Information (Figures S1−S11).

Subsequently, employing the phosphorylation technique described by Yamazaki et al.,⁶³ a series of DBCOD-containing main-chain polyarylamides were prepared from compound 5 (DBCOD-COOH), 4,4′-oxydibenzoic acid (OBA), and 3,4′-oxydianiline (ODA) by the direct polycondensation with triphenyl phosphate (TPP) and pyridine as condensing agents in N-methyl-2-pyrrolidone (NMP) solution containing CaCl₂. 3,4′-ODA instead of 4,4′-ODA was chosen because the resulting a mixture of para- and meta-substituted amides could offer a less crystalline structure that can facilitate the DBCOD conformational change.⁶⁴ OBA was employed to regulate the amount of DBCOD in the polymer. The feeding molar ratio of monomers OBA:DBCOD-COOH:ODA was 1:0:1, 2:1:3, 1:1:2, 1:2:3, and 0:1:1; the resulting polymers are denoted as OBAODA, DBODA1, DBODA2, DBODA3, and DBODA4, respectively. All the polymerizations proceeded homogeneously throughout the reaction and afforded clear, highly viscous polymer solutions. The isolated polymers...
Table 2. Thermal Properties and Mechanical Properties for the Prepared DBODA Copolymers

<table>
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<td>$T_g$ (°C)</td>
<td>$T_{LAM}$ (°C)</td>
<td>$T_L$ (°C)</td>
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$^a$Glass transition temperatures were recorded by DSC for the second heating scan at a rate of 10 °C/min. $^b$Decomposition temperature at 5% or 10% weight loss were recorded by TGA at a heating rate of 20 °C/min and nitrogen flow rate of 40 mL/min. $^c$Mechanical properties were tested with an Instron 5565 mechanical testing instrument with a load cell of 500 N.

Figure 3. Thermal contraction behavior for the prepared DBODA copolymer films. (a) TMA plots for the series of DBODA films by a heating rate of 2 °C/min. (b) TMA plots for DBODA3 film at various heating rates.

showed good solubility in high polar solvents such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and NMP. Weight-average molecular weights ($M_w$) and number-average molecular weights ($M_n$) were determined by a gel permeation chromatography (GPC) (Figure S12) to be in the ranges of 17 100–33 600 g/mol and 11 100–17 900 g/mol, respectively, relative to poly(methyl methacrylate) (PMMA) standards. Structural features of these polyarylamides were verified by spectroscopic analysis using $^1$H NMR and FT-IR (Figure 2). The resonance signals at δ 3.20 ppm assigned to the methylene of DBCOD increased with the feeding molar ratio of DBCODs, and the resonance intensity ratios of –NH– proton signals at δ 10.27 ppm to δ 10.07 ppm were in accordance with theoretical feeding ratios (Table 1). FT-IR spectra exhibited characteristic amides group absorption bands around 3425 and 3310 cm$^{-1}$ (–NH– stretching), 1654 cm$^{-1}$ (amide carbonyl stretching), and 1601 cm$^{-1}$ (–NH– deformation), further demonstrating the successful preparation of functional polyarylamides. The detailed synthetic results for the prepared polymers are shown in Table 1. The amount of DBCOD units was 15.5%, 22.6%, 29.4%, and 42.0% in the polymers of DBODA1, DBODA2, DBODA3, and DBODA4, respectively. OBAODA with no DBCOD was prepared as the control.

Thermal and Mechanical Properties of the Prepared Polyarylamides. Thermal properties of the as-prepared linear polyarylamides were investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results are summarized in Table 2, and representative curves are presented in Figures S13 and S14. All of the polyarylamides exhibited good thermal stability up to 450 °C in a nitrogen atmosphere. The temperatures for 5% and 10% weight loss were observed in the ranges of 452–481 and 502–526 °C, respectively. DSC analysis showed glass transition temperatures ($T_g$) in the range 244–261 °C, which slightly increased with the amount of DBCOD content. This is due to the reduction of the content of OBA that has a lower rotation barrier than DBCODs. Unlike the first generated DBCOD-containing polymers where DBCODs are at the cross-linking positions, this linear DBCOD polyarylamide can be solution-processed (Figure S15). The prepared films exhibited low light absorption in the visible and NIR regions (800–1200 nm) according to the UV–vis–NIR spectroscopic analysis shown in Figure S16. Moreover, the light absorption at a wavelength less than 500 nm increased with OBA content. The $\pi$–$\pi^*$ transition originated from the conjugation between the aromatic rings and oxygen atoms of OBA is ascribed to the increased photon absorption. The tensile properties (Table 2) of these films were tested on an Instron 5565 mechanical testing instrument. All films showed high tensile strength of 73–84 MPa, initial modulus of 6.3–8.8 GPa, and elongation at break of 4.8–6.2%. These values suggested that the new polyarylamide films are mechanically strong.43

Thermal Expansion/Contraction Behavior Investigation. Thermomechanical analysis (TMA) was employed to study thermal responsive behavior by monitoring the length change of DBCOD-containing polyarylamide films as a function of the temperature range of 30–200 °C, which is below $T_g$. The thermal expansion/contraction ratio ($\Delta L/L_0$) vs temperature is plotted in Figure 3a. The average values of CTE are calculated eq 1 and displayed in Table S1. The OBAODA control showed almost a linear increase of $\Delta L/L_0$ with temperature at a heating rate of 2 °C/min, with the average CTE of 91.8 ppm/K (30–200 °C). In contrast, polymers incorporating DBCOD units showed thermal contraction at a temperature greater than 75 °C. The maximum contraction varied from 1.50% to 7.38%. Among all the tested polymers, DBODA3 provided the highest thermal contraction value, with the maximum contraction ratio of 7.38% at 2 °C/min and CTE of $-624.7$ ppm/K (100–200 °C).
We further examined the effect of heating rate on thermal contraction. From Figure 3b and Table S2, we can see that the CTE value of DBODA3 increased with decreasing heating rate from 10 to 1 °C/min. There is no difference between 0.5 and 1 °C/min heating rate. The maximum contraction is about 10%, inferring that the equilibrium can be established under 1 °C/min. Furthermore, DBODA2 was used to examine the reversibility. DBODA2 was first heated to 200 °C at a heating rate of 5 °C/min and then cooled down to room temperature. After holding at 40 °C for a designed period of time, TMA measurements were recorded (Figure 4a). The recovery ratio is defined as the ratio of the contraction value at a given interval of time to the initial contraction value ratio. 93.6% recovery after 42 h can be obtained (Figure 4b). Results indicate that the thermal contraction was almost reversible. It requires long enough time for molecular motion to cross over energy barrier and polymer chain relaxing at a temperature far below than \( T_g \).

It is worth pointing out that DBODA4 which possesses the highest amount of DBCODs does not offer the highest NTE values. This might be because that the DBCOD local environment can play an influential role as indicated in our previous work.\(^{25}\) The wide-angle X-ray diffraction (WAXD) analysis was employed to study crystallinity for the series of polymer films. DBODA2 and DBODA3 exhibited broad amorphous halos at 2\( \theta \) between 15° and 30°, indicative of lack of crystalline structures (Figure S17). Meanwhile, OBAODA, DBODA1, and DBODA4 polymer film patterns exhibited stronger reflections in the same range. Surface morphology was studied by atomic force microscope (AFM) under the tapping-mode, and the phase and height images (2 \( \mu m \times 2 \mu m \)) were recorded (Figure S18). Compared with OBAODA, DBODA1, and DBODA4, the morphology of DBODA2 and DBODA3 polymer films showed smooth surface, which meant the weak interaction of the polymer chains. Together with WAXD analysis, DBODA3 polymer films were more disordered compared with DBODA4 due to the presence of OBAs. This amorphous-like morphology can facilitate the DBCOD conformational change therefore resulting in a giant thermal contraction.

**Thermal Contraction Mechanism Study.** To investigate the thermal contraction behavior of the DBCOD-containing polymers at the molecular level, we turned to density-functional theory (DFT) calculations together with variable-temperature NMR spectroscopy (VT-NMR) and DSC. DFT calculations on a single DBCOD-containing model molecule shown in Figure 5 indicate that twist-boat (TB) is the global minimum conformation at room temperature. The activation energy from TB to chair (C, a local minimum) is 8.5 kcal/mol at 298 K, and the relative Gibbs free energy of TB to C is 0.4 kcal/mol at 298 K (Figure 5 and Table S3), much lower than that of the trans\(^{-}\) cis isomerization of azobenzene (activation energy of \( \approx 40 \) kcal/mol and relative Gibbs free energy of \( \approx 12 \) kcal/mol\(^{44}\)). On the other hand, when temperature rises to 473 K, the relative Gibbs free energy of the C conformer is \(-0.7\) kcal/mol lower than the TB conformer because the C conformer possesses higher entropy than the TB conformer (Table S3). Consequently, the equilibrium position shifted to C with temperature increase. In addition, DFT calculations predicted that this conformational change from TB to C could lead to a 15.6% contraction in volume.

Furthermore, VT-NMR spectroscopy has been used to investigate the conformational change as well as equilibrium populations and energies of each conformer of medium size rings.\(^{35-49}\) \(^1\)H NMR measurements were conducted in the range of \(-108\) to 25 °C using 2,9-dicarbaldehyde-substituted-DBCOD (compound 4) as a model molecule in CD\(_2\)Cl\(_2\)–CS\(_2\).
Two peaks appeared at δ 3.28 and δ 3.29 ppm which are assigned to methylene protons of different positions at 25 °C, and new signals around δ 2.69 ppm appeared when the temperature decreased to −65 °C or lower. At −100 °C, there was a 91:9 ratio of the two sets of signals: a singlet for TB (δ 3.50 ppm, δ 3.07 ppm) and AA′BB′ for C (δ 3.22, δ 3.20 ppm and δ 2.71, δ 2.69 ppm). The TB signals further split at −108 °C which is attributed to the resolution of two enantiomer of TB [(+)-TB and (−)-TB] at lower temperatures.47,48 The results indicate that TB is the optimal conformation, with the fraction of 92% at −108 °C.

Then, DSC was used to study the DBCOD conformational interconversion. Figure 7a shows that the DBODA4 preannealed at 120 °C for 12 h indicated an endothermic peak with the onset temperature of 20 °C and peak temperature of 70 °C on 2 °C/min heating rate and endothermic enthalpy of 50.26 J/g, equivalent to 6.01 kcal/mol DBCOD. The measured value is on the same order as the value predicted by DFT calculations, which indicate that the relative enthalpy difference between C and TB is 2.3 kcal/mol at 298 K (Table S3). The discrepancy is due to the fact that DSC measures solid polymers with many DBCOD units whereas DFT uses a single DBCOD molecule.

After resting at 40 °C for 24 h, a similar endothermic enthalpy of 46.11 J/g could be obtained. This is in accordance with TMA recovery test (Figure 4). In addition, there is no noticeable peak in the DSC measurement (Figure 7b) of the OBAODA control polymer without DBCOD units in the same temperature region, further supporting that the DBCOD conformational change is the origin of the endothermic peak.

**CONCLUSION**

In conclusion, we have designed a new synthetic procedure and successfully synthesized a DBCOD-containing monomer and the corresponding linear polyarylamides for the first time. We have demonstrated that DBCOD-based main-chain polymers possessed giant NTE values. This further supports our hypothesis that the observed thermal contraction is due to the DBCOD conformational change from TB to C. Second, we have revealed that the driving force of this new DBCOD polymer system was due to the greater entropy of the chair conformer with temperature increase compared with the twist-boat conformer. Third, we have demonstrated that the DBCOD content and local environment could tune the NTE values. This work provides a pathway for fabricating thermal contracting polymers, which have great potential applications in electronic packaging, photoelectric devices, aerospace engineering, etc.

**ASSOCIATED CONTENT**

1H NMR and 13C NMR spectra of compounds, characterization of polymers (GPC, TGA, DSC, UV−vis−NIR, TMA, XRD, AFM), computational details (PDF)

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**Notes**
The authors declare no competing financial interest.
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