

## Article

# Synthesis of Benzocyclobutene-Capping Liquid Crystalline Poly(ester imide)s with Low Coefficient of Thermal Expansion and Dielectric Constant

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## Abstract

Liquid crystalline poly(ester imide)s (LCPEIs) were synthesized by solution polymerization from 4-hydroxybenzoic acid (4-HBA), 6-hydroxy-2-naphthoic acid (HNA) and *N*-(3-carboxyphenyl)-4-hydroxyphthalimide (3-CHP), with the capping groups of benzocyclobutene (BCB)-containing compounds (BCB-HP for phenolic hydroxyl group and BCB-CP for aromatic carboxylic acid). Subsequent cross-linking of the BCB capping groups upon hot pressing afforded the cured LCPEI films. Optimal properties of these films were achieved by adjusting the capping BCB-HP/BCB-CP contents. These LCPEIs showed favorable thermal properties with a relatively high glass transition temperature ( $T_g$ , 137–167 °C) and low melting temperature ( $T_m$ , 186–194 °C). With the increase in BCB capping content, the tensile modulus, tensile strength, and coefficient of thermal expansion (CTE) exhibited a non-linear tendency of first decreasing and then increasing. LCPEI-3.0 (3 mol% BCB) showed optimal performance: a relatively low CTE ( $20 \times 10^{-6} \text{ K}^{-1}$ ), a relatively high storage modulus (2.55 GPa), a moderate tensile modulus (2.65 GPa), a relatively low dielectric constant ( $Dk = 3.17$ ) with low dielectric loss ( $Df = 0.0034$ ) at 10 GHz, and excellent hydrophobicity (water contact angle = 133°). This improvement embodies an effective strategy to combine advantages of polyester, polyimide, and benzocyclobutene to achieve favorable and excellent comprehensive properties for convenient processability and practical application prospects.

**Keywords:** liquid crystalline polymers; poly(ester imide)s; benzocyclobutene; coefficient of thermal expansion; low dielectric constant

Academic Editor: Alexey Bubnov

Received: 1 February 2026

Revised: 25 February 2026

Accepted: 26 February 2026

Published: 28 February 2026

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## 1. Introduction

With the rapid development of 5G communication, polymers of low dielectric constant ( $Dk$ ) and low dielectric loss ( $Df$ ) have attracted considerable attention, and these polymers also require comprehensive features of excellent thermal and mechanical properties, a low coefficient of thermal expansion (CTE) and a low water absorption rate [1–5]. Liquid crystalline polymers (LCPs) have been known to possess excellent hydrophobicity and a low CTE and maintain very stable dielectric properties of relatively low  $Dk$  and favorably low  $Df$  under high-frequency environments; thus, LCPs are widely considered as ideal materials for antennas in microwave/millimeter-wave frequency

bands [6–8].

Commercial Vectra LCPs (Celanese) condensed from 4-hydroxybenzoic acid (4-HBA) and 6-hydroxy-2-naphthoic acid (HNA) have excellent properties. However, their relatively low and broad glass-transition temperature ( $T_g$ , 50–150°C) and relatively high melting temperature ( $T_m$ , 280 °C) limit their application at higher temperatures and in melt processability [9–12]. The introduction of imide units into the main chain of aromatic polyesters to form liquid crystalline poly(ester imide)s (LCPEIs) can improve their thermal and mechanical properties [13,14]. There have been reports about the introduction of *N*-(3-hydroxy-phenyl)-4-carboxyphthalimide into Vectra-type 4-HBA/HNA co-polyesters and capping the resulting LCPEIs with thermally active groups derived from 4-phenylethynylphthalic anhydride (PEPA) or terminal ethynylphenyl compounds and 3-ethynylaniline (3-EA) to achieve higher  $T_g$  and better mechanical properties [15–17]. However, the curing temperature of these alkyne-type PEPAs was as high as 370 °C, which would limit their practical application [18].

Benzocyclobutene (BCB) is a thermally reactive compound with a low curing temperature, and no small molecules are produced during the curing process [19,20]. According to the Clausius–Mossotti equation [ $Dk = (1 + 2P/V)/(1 - P/V)$ ], the  $Dk$  of a polymer is positively correlated with the volume polarizability ( $P/V$ ), where  $P$  is the molar polarizability and  $V$  is the molar volume, and thus the  $Dk$  of a polymer could be lowered by decreasing the polarizability or increasing the molar volume of the polymer [21–25]. BCB has an all-hydrocarbon structure with low polarity, and the cured eight-membered ring structure increases the molar volume, thus benefiting the dielectric properties [26,27]. There have been strategies to combine polyimide (PI) and BCB to achieve good thermal stabilities or dielectric properties [28–33].

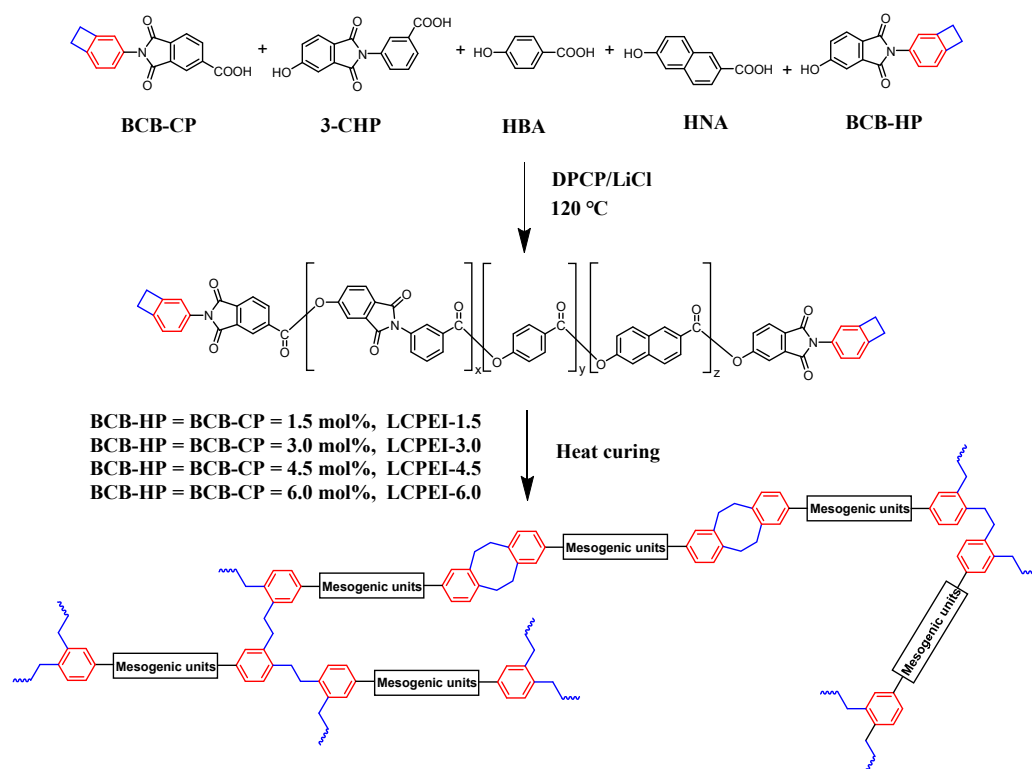
However, the combination of advantages of LCPs and BCB materials has not been reported [34]. Herein, we report the introduction of 4-aminobenzocyclobutene-, 4-hydroxy-phthalic anhydride (HPA)-, and 1,2,4-benzenetricarboxylic anhydride (also known as trimellitic anhydride, TMA)-derived imide compounds; BCB-HP (with phenolic hydroxyl) and BCB-CP (of aromatic carboxylic acid) as capping groups for LCPEI synthesis from 4-HBA, HNA, and *N*-(3-carboxyphenyl)-4-hydroxyphthalimide (3-CHP), with reference to the Vectra A950 LCP (4-HBA/HNA = 73/27); and the relationships of the poly(ester imide)/BCB structure with thermal, mechanical, and dielectric properties. The main objectives aim at improving  $T_g$  and  $T_m$ , to decrease CTE, to enhance hydrophobicity, and to lower  $Dk$  for better processability and practical application reasons.

## 2. Materials and Methods

4-Hydroxybenzoic acid (4-HBA, 98%), 6-hydroxy-2-naphthoic acid (HNA, 98%), 3-aminobenzoic acid (3-ABA, 98%), 4-hydroxyphthalic acid (4-HPA, 98%), and LiCl (99%) were purchased from Shanghai Bide Co. Ltd. (Shanghai, China); 1,2,4-benzenetricarboxylic anhydride (TMA, 97%) was purchased from Anhui Zesheng Co. Ltd. (Hefei, China); diphenyl chlorophosphate (DPCP, 97%) was purchased from Shanghai Aladdin Co. Ltd. (Shanghai, China); 4-amino benzocyclobutene (4-NH<sub>2</sub>-BCB, 94%) was purchased from Wuhan Disai Co. Ltd. (Wuhan, China); and acetic acid, pyridine (Py), methanol and ethanol were purchased from Sinopharm Co. Ltd. (Shanghai, China). 4-Hydroxyphthalic anhydride (HPA) was obtained by sublimation of 4-HPA [35]. *N*-(3-Carboxyphenyl)-4-hydroxyphthalimide (3-CHP) was prepared with HPA and 3-ABA [36]. BCB-HP and BCB-CP were prepared by refluxing HPA or TMA with 4-NH<sub>2</sub>-BCB in acetic acid, respectively [34].

The LCPEIs were synthesized by a solution poly-condensation method as shown in Scheme 1 with LCPEI-3.0 as a general procedure. DPCP (6.917 g, 25.7 mmol) and LiCl (0.807 g, 19.0 mmol) were dissolved in Py (40 mL) and stirred at room temperature for 30

min to obtain a clear Solution A. 3-CHP (1.247 g, 4.4 mmol), 4-HBA (1.408 g, 10.2 mmol), HNA (1.016 g, 2.7 mmol), BCB-HP (80 mg, 0.30 mmol) and BCB-CP (88 mg, 0.30 mmol) were dissolved in Py (20 mL) and heated at 120 °C for 5 min to obtain a clear Solution B. Then, Solution A was added dropwise to Solution B within 10 min, and the resulting mixture was stirred at 120 °C for 5 h. After cooling to room temperature, methanol (100 mL) was added, and the resulting precipitates were filtered and washed with methanol, water and ethanol consecutively. Then, the powder product was collected and dried at 120 °C under vacuum for 12 h until a constant weight of 3.154 g (91% yield) was achieved. Other LCPEIs with different BCB-HP/BCB-CP feed ratios were synthesized similarly and are summarized in Table 1. These LCPEI powders were placed between two polytetrafluoroethylene (PTFE) sheets and pressed in preheated hot steel plates at 250 °C for 30 min with a pressure of 8 MPa. After cooling to room temperature, the resulting films were then cured in an oven at 230 °C/1 h + 250 °C/1 h + 270 °C/1 h + 290 °C/1 h. The thickness of the cured LCPEI films measured 80–150 µm (by a digital thickness gauge).



**Scheme 1.** Synthetic route of the LCPEIs.

**Table 1.** Preparation recipes and inherent viscosity (I.V.) of the LCPEIs.

| Sample    | Feed Ratio (mol%) |     |       |        |        | I.V. (dL/g) |
|-----------|-------------------|-----|-------|--------|--------|-------------|
|           | HBA               | HNA | 3-CHP | BCB-CP | BCB-HP |             |
| LCPEI-1.5 | 51                | 27  | 22    | 1.5    | 1.5    | 0.61        |
| LCPEI-3.0 | 51                | 27  | 22    | 3.0    | 3.0    | 0.48        |
| LCPEI-4.5 | 51                | 27  | 22    | 4.5    | 4.5    | 0.41        |
| LCPEI-6.0 | 51                | 27  | 22    | 6.0    | 6.0    | 0.28        |

Fourier infrared spectroscopy (FTIR) spectra were recorded using a Bruker TENSOR 27 spectrometer (Ettlingen, Germany) in the 600–4000 cm<sup>−1</sup> wave number range. <sup>1</sup>H NMR was tested using a Bruker AVANCE III 400 NMR spectrometer, and the LCPEIs were dissolved in CDCl<sub>3</sub> and pentafluorophenol (PFP) (*v/v* = 4/1) with tetramethylsilane

(TMS) as the internal standard. The inherent viscosities (I.V.s) of the LCPEIs were measured in  $\text{CHCl}_3/\text{PFP}$  ( $v/v = 4/1$ ) (0.5 g/dL at 30 °C). Wide-angle X-ray diffraction (WAXD) or X-ray diffraction (XRD) patterns were recorded in the range of  $2\theta = 5\text{--}60^\circ$  using Panalytical X'pert powder (Cu-K $\alpha$  radiation source) (Malvern, UK). Thermogravimetric analysis (TGA) was conducted on TA TGA55 (New Castle, DE, USA) at 40–800 °C with a heating rate of 20 °C/min under  $\text{N}_2$ . The  $T_g$  of the LCPEIs was measured by differential scanning calorimetry (DSC) on TA Q20 at 40–350 °C with a heating rate of 20 °C/min under  $\text{N}_2$ . The liquid crystalline phase behaviors were observed by a Sunny CX40P polarized optical microscope (POM) (Ningbo, China) equipped with a hot stage with a heating rate of 40 °C/min. The tensile modulus, tensile strength, and elongation at break of the LCPEI films were tested using a Szssans CMT6503 electronic testing machine (Ningbo, China) at a strain rate of 5 mm/min. Dynamic Mechanical Analysis (DMA) was measured by Netzsch DMA242E in tensile mode and in air from 30 to 150 °C at a heating rate of 5 °C/min with a frequency of 1 Hz, a preload force of 20 mN and an amplitude of 5  $\mu\text{m}$ . The CTE was measured with TA Q400 from 30 to 150 °C at a heating rate of 5 °C/min with a preload force of 0.2 N under tensile modeling. The dimensions of each LCPEI film were  $(30 \pm 0.2) \text{ mm} \times (5 \pm 0.2) \text{ mm} \times (0.15 \pm 0.05) \text{ mm}$ . The water absorption of the LCPEI films was deduced by weight changes before and after immersion in deionized water at 25 °C for 24 h, and larger film samples ( $>0.2 \text{ g}$ ) were required to reduce experimental errors. The contact angle was measured using a DSA25 (KRÜSS, Hamburg, Germany) contact angle measuring device with distilled water. Dielectric properties ( $D_k$  and  $D_f$ ) were measured using a QWED SPDR (Warsaw, Poland) (split post dielectric resonator) and Keysight P9373B VNA (Santa Rosa, CA, USA) (vector network analyzer) at 10 GHz (25 °C, air humidity 40–50%) by following the IPC-TM-650 2.5.5.15 method ([www.electronics.org](http://www.electronics.org)).

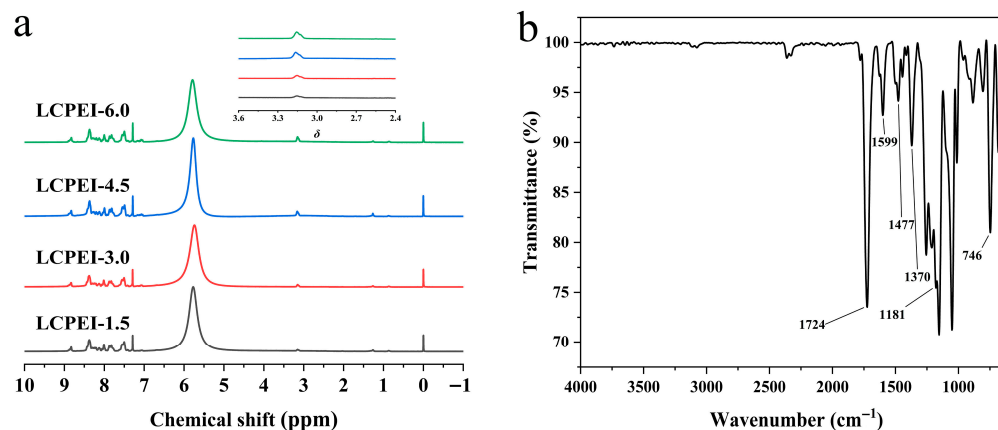
### 3. Results and Discussion

#### 3.1. Polymerization and Characterization

Compared to the traditional melt poly-condensation, which requires high temperatures and high vacuum [37], the solution polymerization could be conducted at lower and operable temperatures following the Higashi–Yamazaki poly-condensation method [38]. We kept the molar fraction of HNA in Vectra LCP at 27 mol%, while 4-HBA was partially replaced by 3-CHP (22 mol%). These LCPEIs based on 4-HBA, HNA, 3-CHP, and BCB-HP/BCB-CP were synthesized in the presence of DPCP, LiCl, and Py at 120 °C, as shown in Scheme 1. The BCB-HP and BCB-CP were introduced to reduce the molecular weights by capping the molecular chain and improved the solubility of the LCPEIs. The Vectra LCPs are difficult to dissolve in most organic solvents except corrosive solvents such as PFP, whereas the LCPEIs obtained herein are soluble in  $\text{CHCl}_3/\text{PFP}$  ( $v/v = 4/1$ ). The relatively decreased molecular weights and the distorted structure of the imide portion might have contributed to improving the solubility. As shown in Table 1, the I.V. of the LCPEIs decreased remarkably from 0.61 to 0.28 with an increase in the BCB capping content from 1.5 to 6.0 mol%. The improved solubility facilitated structural characterizations of the LCPEIs. However, because of the corrosive nature of PFP, gel permeation chromatography (GPC) and MALDI-TOF Mass Spectrometry analysis might not be viable in the present study.

Figure 1a shows the  $^1\text{H}$  NMR spectra of the LCPEIs containing BCB capping groups. All the LCPEIs have similar and characteristic signals of aromatic ring hydrogen at chemical shifts of 6–9 ppm, and the characteristic peak of  $-\text{CH}_2\text{CH}_2-$  appears at 3.16 ppm (on the upper right). With the increase in the BCB capping group content in the LCPEIs, the integral area at 3.16 ppm increases gradually, indicating that the BCB groups have been successfully incorporated into the LCPEIs. As shown in Figure 1b, the FTIR ab-

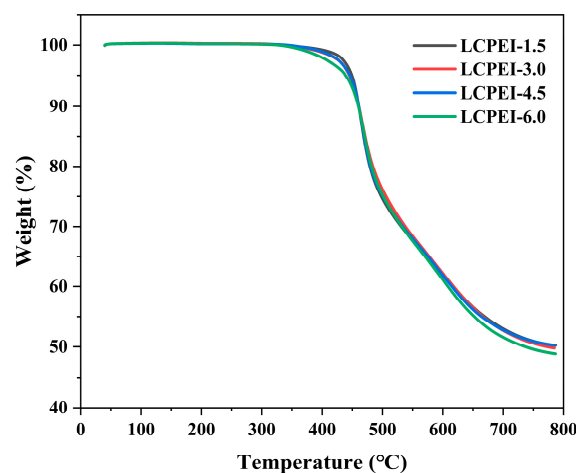
sorption peak of the ester carbonyl group appears at  $1724\text{ cm}^{-1}$ , which partially overlaps with the  $\text{C=O}$  stretching vibration peak of the imide group. The bending vibration peak of the imide group is at  $746\text{ cm}^{-1}$ , and the band at  $1370\text{ cm}^{-1}$  is due to the  $\text{C-N}$  stretching vibration. The peaks at  $1477$  and  $1181\text{ cm}^{-1}$  are absorption peaks of  $-\text{CH}_2\text{CH}_2-$ , which overlap with the absorption peaks of the naphthalene ring in HNA.



**Figure 1.** (a)  $^1\text{H}$  NMR and (b) FTIR spectra of the LCPEIs.

### 3.2. Study of Thermal Properties of the LCPEIs

The TGA results of the LCPEIs are shown in Figure 2, and their thermal properties are summarized in Table 2. The 5% weight loss temperature ( $T_{d5\%}$ ) of all the LCPEIs under  $\text{N}_2$  was in the range of  $438.5$ – $449.3\text{ }^\circ\text{C}$ , and the high residual carbon rate ( $\sim 50\text{ wt}\%$ ) at the high decomposition temperature of  $800\text{ }^\circ\text{C}$  indicated that these LCPEIs have excellent thermal stability. With the increase in BCB capping group content, the thermal stability of the LCPEIs tends to decrease, presumably due to the fact that the aliphatic eight-membered ring formed by the ring opening and chain extension of BCB is more prone to decomposition at higher temperatures than the benzene ring [39].



**Figure 2.** TGA curves of the LCPEIs.

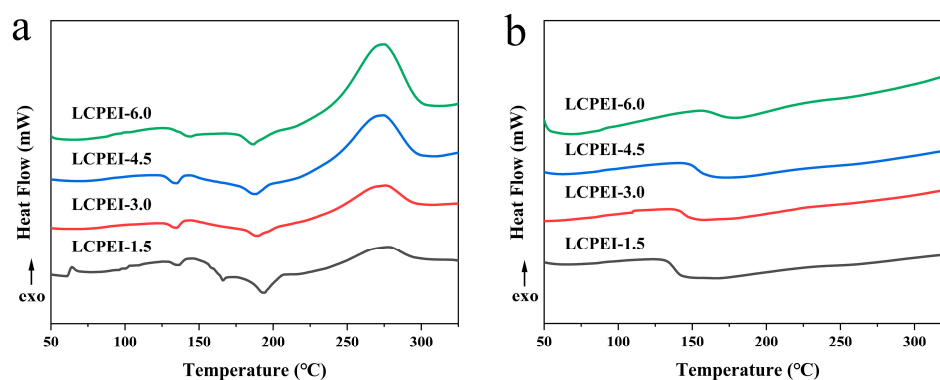
**Table 2.** Thermal properties of the LCPEIs.

| Sample    | $T_g$ (°C) <sup>1</sup> | $T_g$ (°C) <sup>2</sup> | $T_m$ (°C) <sup>1</sup> | $T_m$ (°C) <sup>3</sup> | $T_{d5\%}$ (°C) | $R_{w800}$ (%) <sup>4</sup> |
|-----------|-------------------------|-------------------------|-------------------------|-------------------------|-----------------|-----------------------------|
| LCPEI-1.5 | 137                     | 135                     | 194                     | 200                     | 449.3           | 50.2                        |
| LCPEI-3.0 | 144                     | 145                     | 190                     | 200                     | 445.1           | 49.8                        |
| LCPEI-4.5 | 153                     | 148                     | 188                     | 200                     | 446.0           | 50.2                        |
| LCPEI-6.0 | 167                     | 161                     | 186                     | 200                     | 438.5           | 48.9                        |

<sup>1</sup> Detected by DSC; <sup>2</sup> determined by TMA; <sup>3</sup> determined by POM; <sup>4</sup> mass carbon residual rate at 800 °C.

As shown in Table 2, the four LCPEIs have multiple melting peaks, and the highest  $T_m$  of the four LCPEIs is in the range of 186–194 °C. This phenomenon may be attributed to the wide molecular weight distribution due to the solution poly-condensation reaction, and the melting points of the LCPEIs with different molecular weights are not the same. With the increase in the BCB capping group content (from 1.5 to 6.0 mol%), the  $T_m$  of the LCPEIs showed a decreasing trend, but this trend was not large (194–186 °C), while the  $T_g$  showed an increasing trend in a larger range (137–167 °C). The BCB capping groups lowered the molecular weight of the LCPEIs, thus reducing the  $T_m$ , and the twisted imide structure hindered the stacking arrangement of the molecular chains in the lattice, further lowering the lattice energy to reduce the  $T_m$  [40]. The BCB capping groups successfully played a role in lowering the  $T_m$  and elevating the  $T_g$  of the LCPEIs.

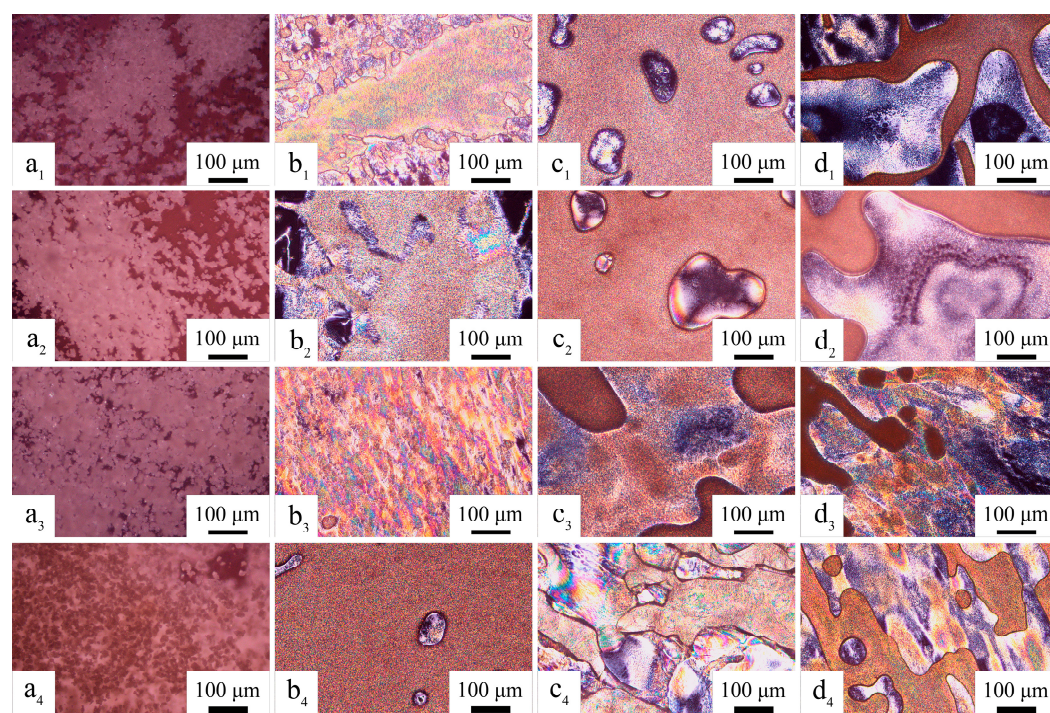
As shown in Figure 3a, during the first heating process, a broad exothermic peak (corresponding to the BCB ring opening and chain extension reaction) appeared in the range of 230–300 °C (peaking at 270 °C), and the exothermic peak gradually increased with the increase in BCB capping group content in the LCPEIs. Figure 3b shows that the exothermic peak disappeared during the second heating cycle, which indicates that the curing of the LCPEIs with BCB capping groups can be completed below 300 °C, which is remarkably lower than the LCPEIs with PEPA-derived capping groups (370 °C).

**Figure 3.** DSC curves of the LCPEIs for (a) the 1st heating and (b) the 2nd heating.

As shown in Figure 4, the LCPEIs melt at around 200 °C, which is close to the highest melting temperature in DSC. At this temperature, the LCPEIs transformed from a solid phase to a liquid crystalline phase and behaved as a nematic melt. Combined with the  $T_m$  measured by DSC in Table 2, we conclude that the increase in BCB capping group content does further reduce the  $T_m$ , which might help to improve the processability of the LCPEIs.

When the temperature increases and the heating time prolongs, the fluidity of the liquid crystal melts gradually weakens for the samples. Some of the melts adhere to the glass plate with a dwindling flowingness. This phenomenon corresponds to the ring opening and chain extension of BCB to increased molecular weights, a higher melt vis-

cosity and weakened fluidity with the prolongation of heating time. However, the resulting flexible eight-membered ring structure could also make the aromatic ring deviate from the linear co-planar structure, change the local rigid rod-shaped structure of the LCPEIs, and reduce the stability of the liquid crystalline phase. With fewer end-capping BCBs, LCPEI-1.5 could complete the ring opening and chain extension reaction faster and disrupt the original orientational order more quickly within the same time frame, as evidenced by more isotropic liquid phases and fewer liquid crystalline phases with birefringence (Figure 4(d<sub>1</sub>)) compared to other samples (cf. LCPEI-6.0, Figure 4(d<sub>4</sub>)).

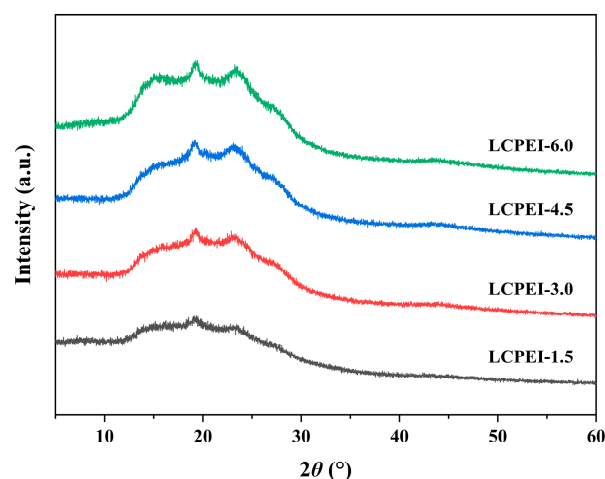


**Figure 4.** POM images of (a<sub>1</sub>–d<sub>1</sub>) LCPEI-1.5, (a<sub>2</sub>–d<sub>2</sub>) LCPEI-3.0, (a<sub>3</sub>–d<sub>3</sub>) LCPEI-4.5 and (a<sub>4</sub>–d<sub>4</sub>) LCPEI-6.0 ((a<sub>1</sub>–a<sub>4</sub>), 150 °C; (b<sub>1</sub>–b<sub>4</sub>), 200 °C; (c<sub>1</sub>–c<sub>4</sub>), 300 °C; (d<sub>1</sub>–d<sub>4</sub>), 350 °C); scale bar = 100 μm.

### 3.3. WAXD Analysis

As shown in Figure 5, with the same 3-CHP content, the diffraction peak types and  $2\theta$  angle positions of the four LCPEIs essentially are of the same pattern, thus implying that the  $2\theta$  values of the LCPEIs are related to the 3-CHP content but not to the BCB capping group content. There are weak diffraction peaks of the LCPEIs at  $2\theta = 14.0^\circ$ ,  $19.3^\circ$ ,  $23.2^\circ$ , and  $26.8^\circ$ . Compared to references [12,41], the last three peaks correspond to (110), (200), and (004) crystal planes, respectively, indicating that the LCPEIs exhibit a crystalline structure and belong to the orthorhombic crystal system.

It is obvious that the introduction of BCB capping groups could increase the intensity of the diffraction peaks of the LCPEIs, and the reason for the increase in the diffraction peak intensity might be due to a higher BCB capping group content, which gradually reduces molecular weights of the LCPEIs. The crystalline regularity of shorter molecular chains is higher than longer molecular chains, thus resulting in stronger diffraction peak intensity.



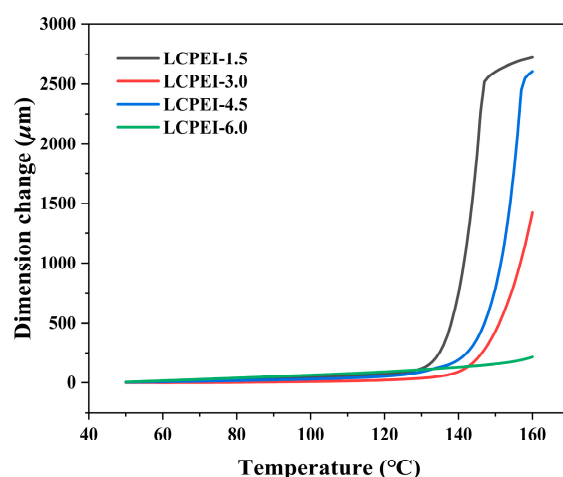
**Figure 5.** WAXD patterns of the LCPEIs.

### 3.4. Study of Mechanical Properties of the LCPEI Films

The mechanical properties and CTE of the LCPEI films are shown in Table 3. The DMA results show that introducing BCB capping groups within a given range and curing could improve the storage modulus of the LCPEI films (2.55 vs. 2.43 GPa). However, the storage modulus of the LCPEI films changes abruptly and decreases instantaneously (from 2.43 to 0.15 GPa) when the BCB capping group content is higher than a threshold ( $\geq 6$  mol%). The TMA curves of the LCPEI films are shown in Figure 6, and the CTE decreases significantly with an appropriate increase in BCB capping group content. However, as the BCB capping group content continues to increase, the CTE of the LCPEI films reverses and increases gradually. The V-shaped overall trend indicates that the BCB capping groups can indeed play a role in reducing the CTE, and an optimal BCB capping content (3.0 mol%) can achieve a favorable CTE ( $20.46 \times 10^{-6} \text{ K}^{-1}$ ) for better dimensional stability [42].

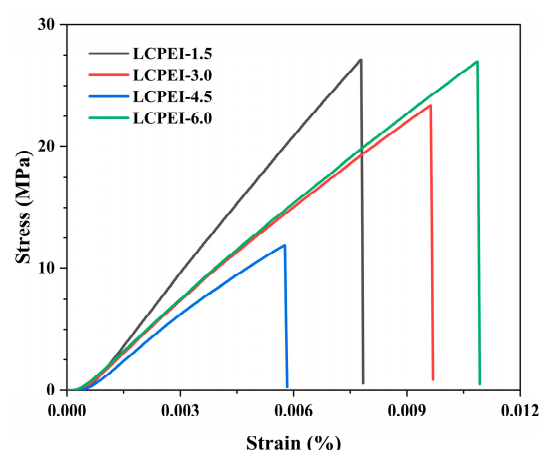
**Table 3.** Mechanical properties of the LCPEI films.

| Sample    | Tensile Modulus (GPa) | Tensile Strength (MPa) | Elongation at Break (%) | $E'$ (GPa) | CTE ( $10^{-6} \text{ K}^{-1}$ ) |
|-----------|-----------------------|------------------------|-------------------------|------------|----------------------------------|
| LCPEI-1.5 | 4.83                  | 27.13                  | 0.75                    | 2.43       | 68.55                            |
| LCPEI-3.0 | 2.65                  | 23.37                  | 0.88                    | 2.55       | 20.46                            |
| LCPEI-4.5 | 2.61                  | 11.86                  | 0.86                    | 2.53       | 50.77                            |
| LCPEI-6.0 | 3.36                  | 26.97                  | 1.18                    | 0.15       | 82.98                            |



**Figure 6.** TMA curves of the LCPEIs.

Figure 7 shows the stress–strain curves of the LCPEI films. The shape of the curve indicates that the materials exhibit hard and brittle properties, with a low elongation at break. As shown in Table 3, the tensile modulus and tensile strength of the LCPEIs show a trend of first decreasing and then increasing; the larger the tensile modulus, the stronger the resistance to deformation. The reason for the decrease in the tensile modulus after introducing BCB capping groups may be the formation of a flexible eight-membered ring structure after the BCB ring opening and chain extension, which reduces the rigidity of the chain segments. The tensile strength and elongation at break of these LCPEI films are relatively low, and this phenomenon may be caused by processing. In addition to the molecular structure and compositional factors, the material properties are closely related to the thermal and mechanical processing history, processing equipment and process methods. The melting liquid crystal materials are in easy orientation, and perpendicular to the direction of the orientation of the stress are very easy to tear. LCP films prepared by hot pressing may be due to instrumental errors that lead to the film thickness and orientation direction not being uniform and regular, while films prepared by blowing and bi-directional stretching method can effectively improve the anisotropy, insufficient flexibility and other shortcomings. However, the blowing/stretching processes are complicated and require delicate equipment. Although the flexible eight-membered ring structure formed by the ring opening and chain extension of BCB capping groups reduces the tensile strength, the presence of the flexible structure also slightly improves the elongation at break of the film (0.75–1.18%).



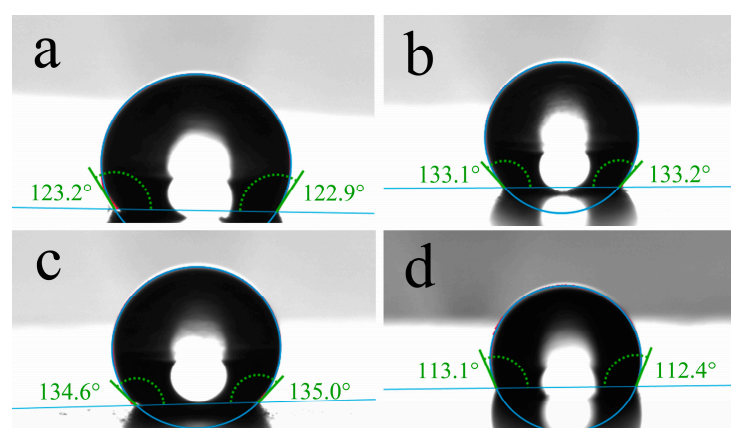
**Figure 7.** Stress–strain curves of the LCPEIs.

### 3.5. Hydrophobicity and Dielectric Properties of the LCPEIs

The substrate materials for high-frequency and high-speed communication devices require good dielectric properties (low  $D_k$  and  $D_f$ ) and a lower water absorption due to water's destructively high  $D_k$  (78 at 25 °C) [43–45]. The hydrophobicity of the LCPEI films was characterized by the contact angle test. As shown in Figure 8 and Table 4, with higher BCB capping group content, the contact angle gradually increases, implying gradually enhanced hydrophobicity. However, when the BCB capping group content exceeds a certain threshold ( $\geq 4.5$  mol%), the contact angle decreases, reversing to a reduced hydrophobicity. A more direct water absorption test was performed, as shown in Table 4. With the increase in BCB capping group content, the water absorption rate gradually rises and then decreases, but the overall rate is still low (0.18–0.54%). The rigid ester group and the close molecular chain stacking in LCPs are the main reasons for the low water absorption, but with the increase in the imide content, the rigidity of the molecular chain in the LCPEIs decreases, thus hindering the lateral stacking of the polyester molecular chains, which makes the water absorption of the LCPEI films gradually in-

crease. Herein, an optimal BCB capping content (3.0 mol%) can achieve a favorably low water absorption rate.

However, dielectric properties at 10 GHz show no obvious trend, with a relatively higher  $Dk$  (3.55) for LCPEI-1.5 and a relatively lower  $Dk$  (3.17) for LCPEI-3.0 and a narrow range of  $Df$  (0.0032–0.0036). The reason for varied  $Dk$  and  $Df$  may be attributed to two aspects: on one hand, the imide units have a strong dipole moment, and on the other, the molecular weight of the solution polymerization method is less than that of the melt poly-condensation method. However, the imide part might contribute to a better  $Dk$ , and BCB capping groups for chain extension might achieve higher molecular weights. Despite multiple interaction factors, dielectric properties of the LCPEI films still meet the range of low dielectric materials, comparable to Kuraray's Vecstar™ LCP films ( $Dk = 3.3$  and  $Df = 0.002$ ).



**Figure 8.** Contact angles of (a) LCPEI-1.5, (b) LCPEI-3.0, (c) LCPEI-4.5 and (d) LCPEI-6.0.

**Table 4.** Water absorption and dielectric properties of the LCPEI films.

| Sample    | Contact Angle (°) | Water Uptake (%) | $Dk$ (@10 GHz) | $Df$ (@10 GHz) |
|-----------|-------------------|------------------|----------------|----------------|
| LCPEI-1.5 | 123.2             | 0.18             | 3.55           | 0.0032         |
| LCPEI-3.0 | 133.2             | 0.27             | 3.17           | 0.0034         |
| LCPEI-4.5 | 135.0             | 0.54             | 3.36           | 0.0032         |
| LCPEI-6.0 | 113.1             | 0.37             | 3.28           | 0.0036         |

## 4. Conclusions

In this study, BCB-type capping groups (phenolic hydroxyl BCB-HP and aromatic carboxylic acid BCB-CP) of relatively low curing temperature ( $<300$  °C) have been introduced into the modified Vectra-type LCP (4-HBA/HNA/3-CHP) to form new LCPEIs. These LCPEIs have relatively high  $T_g$  and low  $T_m$ , which are desirable features for friendly processability. LCPEI-3.0 is optimal for its favorably low CTE of  $20 \times 10^{-6}$  K $^{-1}$ , excellent hydrophobicity (a contact angle of  $133^\circ$ ), and promising dielectric properties ( $Dk = 3.17$  and  $Df = 0.0034$  at 10 GHz). This effective strategy to combine advantages of polyester, polyimide, and benzocyclobutene has contributed to achieving favorable properties for practical implications.

**Author Contributions:** Conceptualization, Z.H.; methodology, S.P., W.W., X.W. and H.G.; resources (funding), H.Y., J.L. and X.L.; writing—original draft preparation, W.W. and S.P.; writing—review and editing, Z.H.; supervision, H.Y., J.L., Z.H. and X.L. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by JHU (No. 2024XKZ004), the Hubei Provincial Science and Technology Innovation Program (No. 2025BAB032), Wuhan International Science and Technology Cooperation Projects (2025071204030387), the Fundamental Research Funds of Jiangnan University (No. 2023ZDCX01), and a research contract from Wuhan Kenda Kexun Tech. Co., Ltd.

**Data Availability Statement:** The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

**Conflicts of Interest:** The authors declare no conflicts of interest. The funding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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