

Supporting Information

Efficiently predicting and synthesizing intrinsic highly fire-safe polycarbonates with processability

Ronghua Yu,^{a,b} Shengda Wang,^{a,b} Yue Zhu,^{a,b} Qianyu Li,^{a,b} Jiangan You,^{a,b} Jian Qiu,^a Yanhui Wang,^a Jie Liu,^{*a} Tao Tang^{*a,b}

Table of Contents

| | |
|---|-----------|
| 1. Experimental section..... | 2 |
| 1.1 Material genome approach (MGA)..... | 2 |
| 1.2 Synthesis of homopolycarbonates (h-PCs)..... | 3 |
| 1.3 Synthesis of copolycarbonates (co-PCs)..... | 4 |
| 2. Results and Discussion..... | 6 |
| 2.1 Two-step computational high-throughput screening..... | 6 |
| 2.2 Characterization of PCs..... | 10 |
| 2.3 DSC and TGA analysis..... | 14 |
| 2.4 PCFC analysis..... | 15 |
| 2.5 Fire-safe performance..... | 16 |
| 2.6 Transparency of PCs..... | 17 |
| 2.7 Morphology and microstructure of residual chars..... | 17 |
| 2.8 Pyrolysis analysis..... | 19 |
| 3. References..... | 24 |

1. Experimental section

1.1 Material genome approach (MGA)

The structure–property relationship of polymers is used as specific “genetic code” to guide high-throughput screening for balancing and optimizing the following property: fire-safe performance and processability (As shown in Figure S2A, the fire-safety and processability of polymers are a pair of contradictory properties). Importantly, a prerequisite for any structure–property correlation is the ability to identify and reproducibly measure the intrinsic property of interest.¹ Unfortunately, the burning rate, ignitability and heat-release rate of a polymer are not intrinsic properties in the view of polymer flammability.² Therefore, the structure–property correlation is not suitable to be obtained from these extrinsic quantities. The pyrolysis combustion flow calorimetry (PCFC) is an effective method to evaluate the combustibility of milligram samples, and the fire parameters resulting from PCFC, such as total heat release (h_c , kJ/g, refers to the heat of combustion per unit mass of the original polymer), can be used as intrinsic properties of polymers, which are good predictors of fire response and flammability of polymers.

As we know, the largest unique chemical descriptors of polymers are their repeat units that are comprised of chemical groups. One simple method proposed by Van Krevelen to calculate the intrinsic properties of polymers from their chemical groups is the additivity of groups¹:

$$P = \sum_{i=1}^n \sum_{j=1}^n \phi_{ij} P_{ij} = \sum_{i=j} \phi_{ij} P_{ij} + \sum_{i \neq j} \sum \phi_{ij} P_{ij} \quad (\text{S1})$$

Here, P_{ij} is the contribution of groups i and j to property P ($P_{ii}=P_i$, $P_{ij}=(P_i+P_j)/2$); ϕ_{ij} is a dimensionless weighting factor for the interaction between groups i and j ; x_i is the mole, mass or volume fraction of the group i . According to the literature³¹, the interaction terms in Equation S1 are usually ignored ($\phi_{ij}=0$, $i \neq j$). Briefly, the overall property of the polymer is the sum of the specific group contributions multiplied by the mole, mass or volume fraction of the groups. Such an approach has been proposed for the calculation of h_c in PCFC test, and additivity (equation S1) is assumed^{3,4} for chemical groups on a molar basis^{3,4}:

$$h_c = \frac{\sum N_i \Omega_i}{\sum N_i M_i} \quad (\text{S2})$$

Here N_i and M_i are the number of mole and the molar mass of component i , Ω_i is the molar contribution of component i . Figure S2B demonstrates the effectiveness of the molar group contribution method in predicting the value of h_c .

The polymer aggregation state mainly depends on the molecular structure of polymers and the ambient temperature. When the polymer structure is fixed, the aggregate state will depend on the ambient temperature. It is well known that glass transition temperature (T_g) and melting temperature (for crystalline polymers) are two important transition temperatures of polymers, which are closely related to polymer processing performance. For amorphous polymers (such as PC), the T_g is a very important transition temperature. Van Krevelen related the T_g to the chemical structure of polymers through molar group contribution approach¹:

$$T_g = \frac{Y_g}{M} = \frac{\sum N_i Y_{gi}}{\sum N_i M_i} \quad (S3)$$

Here, Y_{gi} is the contribution of group i to T_g ; M is the molecular weight of polymer repeating unit. Finally, the values of h_c and T_g predicted by molar group contribution were used as characteristic indicators for flame retardancy and processability, respectively.

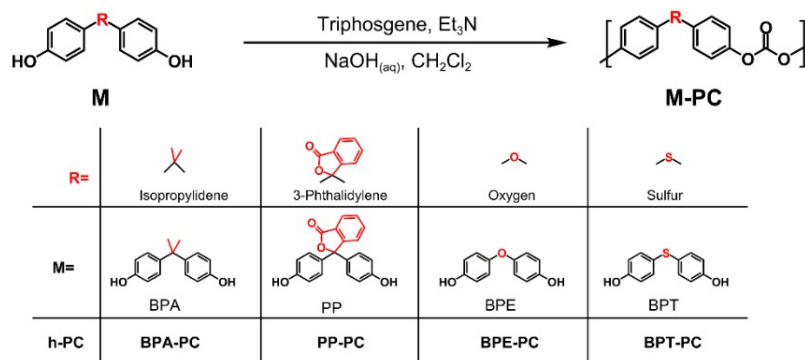
1.2 Synthesis of homopolycarbonates (h-PCs)

1.2.1 Synthesis of phenolphthalein polycarbonate (PP-PC). PP-PC was prepared in a similar manner as BPA-PC in 85% yield. Here Bisphenol A (BPA) was replaced by phenolphthalein (PP). IR (cm^{-1}): 1768 (C=O), 1615~1590 (C-C bond ring stretch), 1218 (O-CO-O), 1080 (Ar-H). ¹H NMR (Chloroform-d, ppm): 7.95 (d, 1H, Ar-H), 7.72 (t, 1H, Ar-H), 7.56 (m, 2H, Ar-H), 7.37 (d, 4H, Ar-H), 7.23 (d, 4H, Ar-H).

1.2.2 Synthesis of 4,4-dihydroxydiphenyl ether polycarbonate (BPE-PC). BPE-PC was prepared in a similar manner as BPA-PC in 77% yield. Here Bisphenol A was replaced by 4,4-dihydroxydiphenyl ether. IR (cm^{-1}): 1767 (C=O), 1593 (C-C bond ring stretch), 1220 (O-CO-O), 1154 (Ar-O-Ar), 1080 (Ar-H). The product was found to be poorly soluble in common solvents (e.g., CHCl_3 , THF, and DMF)

1.2.3 Synthesis of 4,4'-thiodiphenol polycarbonate (BPT-PC). BPT-PC was prepared in a similar manner as BPA-PC in 80% yield. Here Bisphenol A was replaced by 4,4'-thiodiphenol. IR (cm^{-1}): 1767 (C=O), 1584 (C-C bond ring stretch), 1221 (O-CO-O), 1184 (Ar-S-Ar), 1080 (Ar-H). The product was found to be poorly soluble in common solvents (e.g., CHCl_3 , THF, and DMF).

Synthesis of homopolycarbonates (h-PCs):



Synthesis of copolycarbonates (co-PCs):

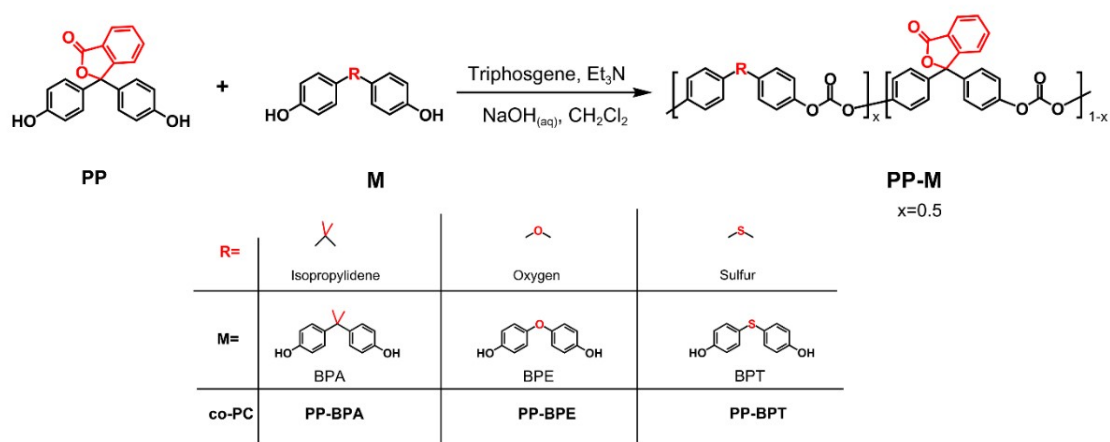


Figure S1. Reaction scheme for the synthesis of h-PCs and co-PCs.

1.3 Synthesis of co-PCs

The polycarbonate copolymers were synthesized by polycondensation of two bisphenol monomers in combination with triphosgene using a similar procedure.

1.3.1 Synthesis of phenolphthalein-bisphenol A copolycarbonate (PP-BPA). Bisphenol A (60 mmol), phenolphthalein (60 mmol), tetrabutylammonium bromide (0.15 mmol) and an aqueous NaOH solution (280 mmol) were added to a 1000 mL four-necked round bottom flask. Under an ice-water bath, triphosgene (48 mmol) dissolved in dichloromethane and TEA (5 mmol) were added to the solution. After the dropwise addition, the ice-water bath was removed and the reaction was carried out at 35 °C for 3 h. The dichloromethane solution was washed with water (three times) and separated. The polymer solution was poured into ethanol, the precipitated product was filtered and washed with ethanol, and the product was dried in a vacuum oven at 80 °C. Yield: 84 %; IR (cm⁻¹): 2969 (CH₃), 1770 (C=O), 1614~1592 (C-C bond ring stretch), 1363 (CH₃), 1224 and 1156 (O-CO-O). ¹H NMR (Chloroform-d, ppm): 7.52-7.97

(Ar-H in PP structure), 7.35-7.41 (Ar-H in PP structure), 7.20-7.29 (Ar-H in BPA and PP structure), 7.12-7.19 (Ar-H in BPA structure), 1.67 (-CH₃). ¹³C NMR (Chloroform-d, ppm): 169.23(C(O)O), 152.14-151.41 ((O-C(O)-O)), 151.32-151.27, 151.07-150.93, 148.95-148.81, 148.47-148.21, 138.76-138.71, 134.48, 129.77, 128.54-128.49, 127.97-127.92, 126.30, 125.39, 124.02, 121.06-121.00, 120.32-120.26, 90.46-90.50, 42.57, 30.92 (CH₃).

1.3.2 Synthesis of phenolphthalein-4,4-dihydroxydiphenyl ether copolycarbonate (PP-BPE). 4,4-dihydroxydiphenyl ether (60 mmol), phenolphthalein (60 mmol), tetrabutylammonium bromide (0.15 mmol) and an aqueous NaOH solution (280 mmol) were added to a 1000 mL four-necked round bottom flask. Under an ice-water bath, triphosgene (48 mmol) dissolved in dichloromethane and TEA (5 mmol) were added to the solution. After the dropwise addition, the ice-water bath was removed and the reaction was carried out at 35 °C for 3 h. The dichloromethane solution was washed with water (three times) and separated. The polymer solution was poured into ethanol, the precipitated product was filtered and washed with ethanol, and the product was dried in a vacuum oven at 80 °C. Yield: 78 %; IR (cm⁻¹): 1767 (C=O), 1614~1593 (C-C bond ring stretch), 1224 and 1156 (O-CO-O). ¹H NMR (Chloroform-d, ppm): 7.52-7.97 (Ar-H in PP structure), 7.35-7.41 (Ar-H in PP structure), 7.20-7.30 (Ar-H in BPE and PP structure), 7.00-7.07 (Ar-H in BPE structure). ¹³C NMR (Chloroform-d, ppm): 169.22 (C(O)O), 155.05-154.93, 151.35-151.43 ((O-C(O)-O)), 151.31, 151.05-150.95, 146.60-146.48, 138.73-138.68, 134.50, 129.80, 128.55, 126.33, 1254.41, 124.03, 122.27-122.22, 121.07-121.02, 119.72-119.66, 90.49.

1.3.3 Synthesis of phenolphthalein-4,4'-thiodiphenol copolycarbonate (PP-BPT). 4,4'-thiodiphenol (60 mmol), phenolphthalein (60 mmol), tetrabutylammonium bromide (0.15 mmol) and an aqueous NaOH solution (280 mmol) were added to a 1000 mL four-necked round bottom flask. Under an ice-water bath, triphosgene (48 mmol) dissolved in dichloromethane and TEA (5 mmol) were added to the solution. After the dropwise addition, the ice-water bath was removed and the reaction was carried out at 35 °C for 3 h. The dichloromethane solution was washed with water (three times) and separated. The polymer solution was poured into ethanol, the precipitated product was filtered and washed with ethanol, and the product was dried in a vacuum oven at 80 °C. Yield: 81 %; IR (cm⁻¹): 1770 (C=O), 1616~1584 (C-C bond ring stretch), 1224 and 1156 (O-CO-O). ¹H NMR (Chloroform-d, ppm): 7.52-7.97 (Ar-H in PP structure), 7.34-7.41 (Ar-H in BPT and PP structure), 7.17-7.28 (Ar-H in BPT and PP structure). ¹³C NMR (Chloroform-d, ppm): 169.22 (C(O)O), 151.61-151.41 ((O-C(O)-O)), 151.27, 150.95-150.92, 150.10-150.06, 138.69, 134.50, 133.51, 132.31-132.25, 129.79, 128.55, 126.34, 125.37, 124.02, 121.79-121.81, 121.04-121.02, 90.47.

2. Results and Discussion

2.1 Two-step computational high-throughput screening

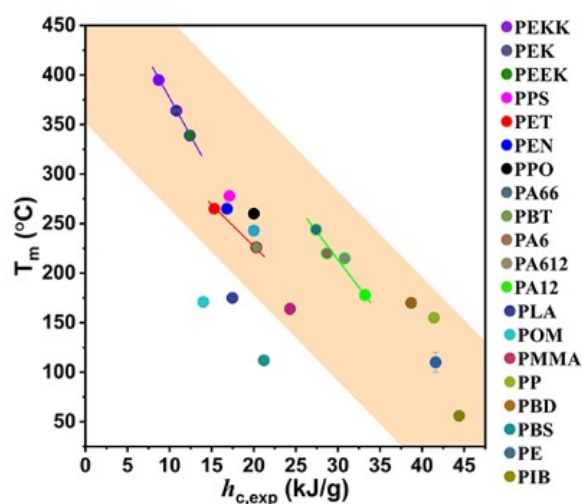


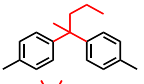
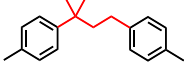
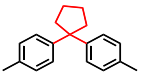
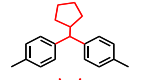
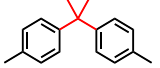
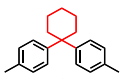
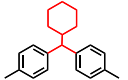
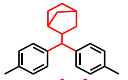
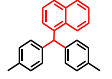
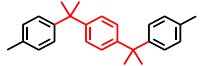
Figure S2. (a) Correlation between heat release and melting point of conventional polymers.

We collected melting temperatures (T_m) for more than 20 kinds of polymers from the SciFinder database, and then plotted T_m values versus heat release ($h_{c,exp}$) measured by PCFC^[3,4] for each polymer. The resulting plot is shown in Figure S2. It can be seen that polymers with lower T_m have higher heat release, such as polyethylene, polypropylene, etc. As expected, polymers with high T_m have lower heat release, such as polyphenylene ether, polyether ketone, etc. In particular, the negative correlation between T_m and $h_{c,exp}$ is more pronounced for a series of polymers with similar groups, such as polyester (PET, PBT), polyether ketone (PEKK, PEK, PEEK) and polyamide (PA12, PA612, PA66, PA6). It is well known that the T_m of crystalline polymers is closely related to their processing temperatures, and heat release can be used as an indicator of fire-safety at the molecular level of polymers. So, the fire-safety and processing properties of polymers are a pair of contradictory properties.

Table S1 Chemical structures, molecular weight and assigned Ω and Y_g values of 36 groups and the calculated $h_{c,cal}$ and $T_{g,cal}$ values of polycarbonate.

| No. | Group | M_i [g/mol] | Ω_i^a [MJ/mol] | Y_{gi}^b [K kg/mol] | Prediction | |
|-----|-------|------------------|--------------------------|--------------------------|-----------------------|---------------------|
| | | | | | $h_{c,cal}$ [kJ/g] | $T_{g,cal}$ [°C] |
| - | | 60.0 | 0.22 | 20 | - | - |
| 1 | | 366.3 | 2.41 | 234 | 6.17 | 322.7 |
| 2 | | 284.3 | 2.40 ^c | 163 ^c | 7.61 | 258.4 |

| | | | | | | |
|----|--|-------|------|-----|-------|-------|
| 3 | | 216.3 | 2.47 | 111 | 9.73 | 201.0 |
| 4 | | 168.2 | 2.28 | 67 | 10.96 | 108.1 |
| 5 | | 152.2 | 2.16 | 70 | 11.22 | 151.0 |
| 6 | | 260.2 | 3.48 | 104 | 11.56 | 114.1 |
| 7 | | 228.3 | 3.24 | 104 | 12.00 | 157.0 |
| 8 | | 228.3 | 3.24 | 111 | 12.00 | 181.2 |
| 9 | | 116.2 | 2.67 | 65 | 12.78 | 102.6 |
| 10 | | 184.2 | 2.94 | 72 | 12.94 | 103.6 |
| 11 | | 278.4 | 4.54 | 138 | 14.07 | 193.8 |
| 12 | | 180.2 | 3.33 | 67 | 14.78 | 89.0 |
| 13 | | 242.3 | 4.32 | - | 15.02 | - |
| 14 | | 242.5 | 4.35 | - | 15.11 | - |
| 15 | | 234.3 | 4.46 | - | 15.89 | - |
| 16 | | 194.3 | 3.84 | - | 15.97 | - |
| 17 | | 266.3 | 5.11 | - | 16.33 | - |
| 18 | | 318.4 | 6.14 | - | 16.81 | - |
| 19 | | 256.3 | 5.15 | - | 16.97 | - |
| 20 | | 208.3 | 4.35 | - | 17.03 | - |
| 21 | | 243.3 | 4.99 | - | 17.18 | - |
| 22 | | 208.3 | 4.50 | - | 17.59 | - |
| 23 | | 346.4 | 7.19 | - | 18.23 | - |
| 24 | | 208.3 | 4.67 | - | 18.23 | - |
| 25 | | 208.3 | 4.67 | - | 18.23 | - |
| 26 | | 374.5 | 7.97 | - | 18.85 | - |

| | | | | | | |
|----|---|-------|------|----|-------|-------|
| 27 |  | 222.3 | 5.18 | - | 19.13 | - |
| 28 |  | 222.3 | 5.18 | - | 19.13 | - |
| 29 |  | 220.3 | 5.20 | - | 19.34 | - |
| 30 |  | 234.3 | 5.54 | - | 19.57 | - |
| 31 |  | 194.3 | 4.79 | 87 | 19.70 | 147.6 |
| 32 |  | 234.3 | 5.71 | - | 20.15 | - |
| 33 |  | 248.4 | 6.05 | - | 20.33 | - |
| 34 |  | 260.3 | 6.88 | - | 22.16 | - |
| 35 |  | 289.3 | 7.67 | - | 22.58 | - |
| 36 |  | 312.4 | 8.50 | - | 23.41 | - |

^aThe Ω_i values were calculated by known group contributions offered by Lyon^{2,3};

^bThe T_{gi} values were calculated by known group contributions offered by Van Krevelen¹;

^cThe Ω_i and T_{gi} values of group 2 were unknown, and the values were assigned by the experimental results (Figure S3).

Among these PCs (Table S1), phenolphthalein-based PCs have highly fire-safety, but the molar group contribution of phenolphthalein group to h_c is unknown. Therefore, we synthesized PC containing phenolphthalein unit (Figure S3a) and measured the total heat release and T_g value of the resultant PC (Figure S3b-3c). Furthermore, we assigned the molar contribution of phenolphthalein group to the total heat release (Figure S3d).

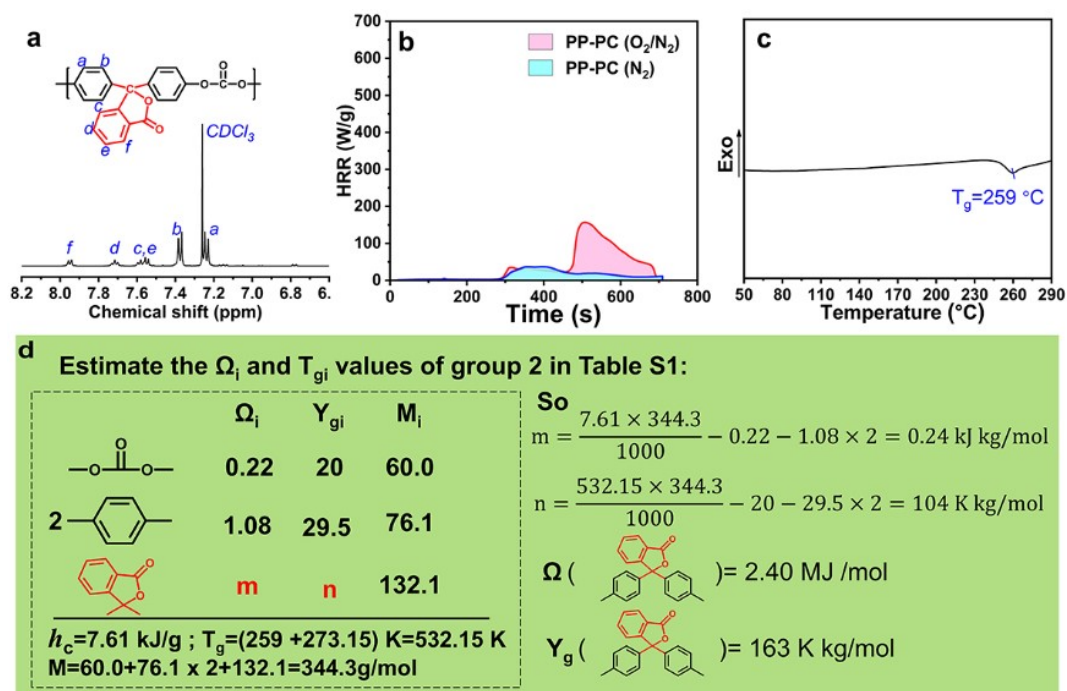
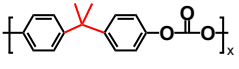
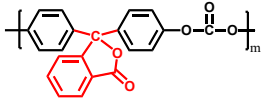
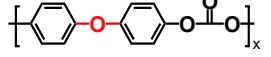
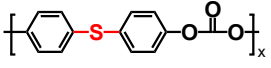
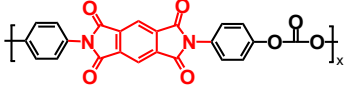
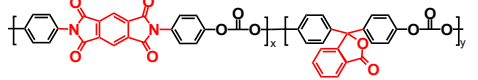
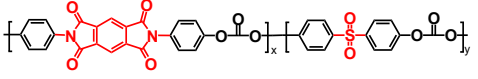
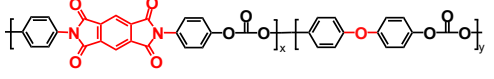
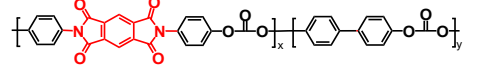
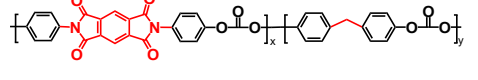
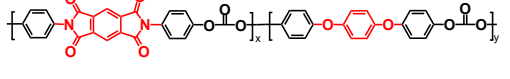
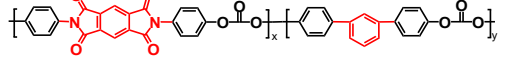
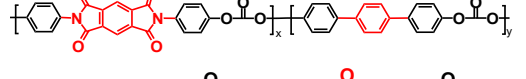
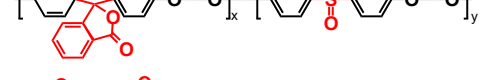
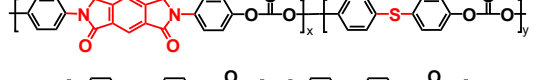
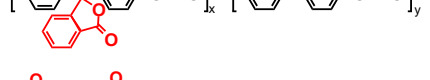
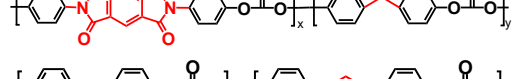
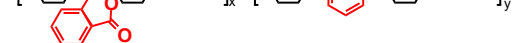


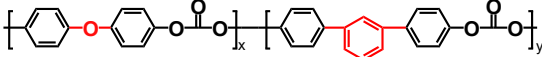
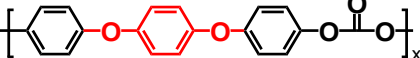
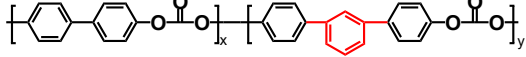
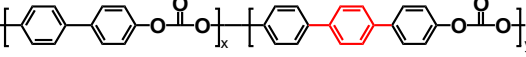
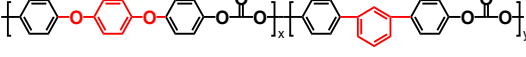
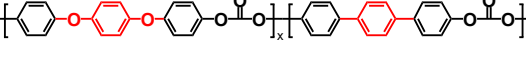
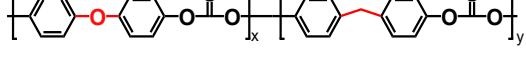
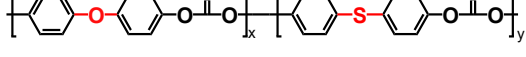
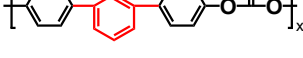
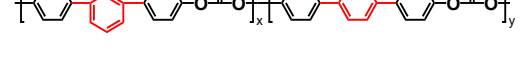
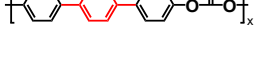
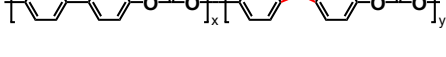
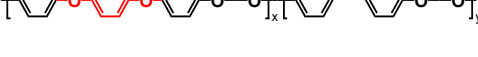
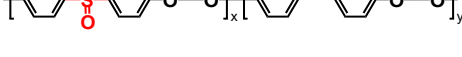
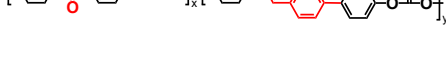
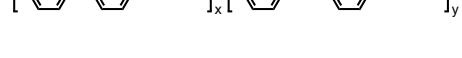
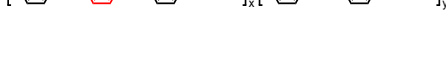

Figure S3. (a) ^1H NMR spectra of PC containing phenolphthalein unit, (b-c) properties of this PC, and (d) estimating the Ω and Y_g values of group 2 in Table S1.

Table S2 Chemical structures and calculated $h_{c,\text{cal}}$ and $T_{g,\text{cal}}$ values of predicted PCs.

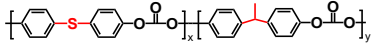
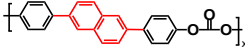
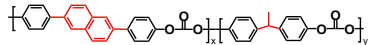
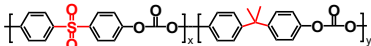
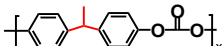
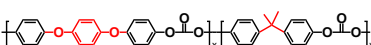
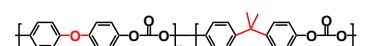
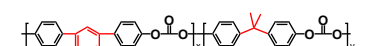
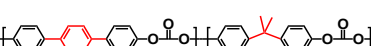
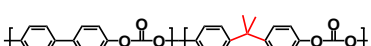
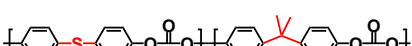

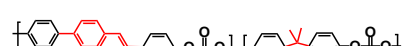
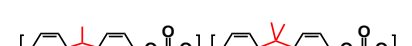
| Optimized structures of PC | | | | |
|----------------------------|---------|------------------|---------------------------|-------------------------|
| No | Name | Structures of PC | $h_{c,\text{cal}}$ [kJ/g] | $T_{g,\text{cal}}$ [°C] |
| 1 | PP-BPE | | 8.94 | 198.5 |
| 2 | PP-BPEE | | 9.51 | 188.9 |
| 3 | PP-BPF | | 9.66 | 196.7 |
| 4 | PP-BPT | | 9.82 | 194.1 |
| Other structures of PC | | | | |
| No | Name | Structures of PC | $h_{c,\text{cal}}$ [kJ/g] | $T_{g,\text{cal}}$ [°C] |
| 5 | PP-BPA | | 12.75 | 211.4 |

| | | | | |
|----|--------|--|-------|-------|
| 6 | BPA-PC |  | 19.70 | 147.6 |
| 7 | PP-PC |  | 7.61 | 258.4 |
| 8 | BPE-PC |  | 10.96 | 108.1 |
| 9 | BPT-PC |  | 12.94 | 103.6 |
| 10 | - |  | 6.17 | 322.7 |
| 11 | - |  | 6.81 | 293.9 |
| 12 | - |  | 7.57 | 274.8 |
| 13 | - |  | 7.84 | 247.8 |
| 14 | - |  | 7.85 | 265.6 |
| 15 | - |  | 8.46 | 246.4 |
| 16 | - |  | 8.48 | 233.2 |
| 17 | - |  | 8.52 | 255.8 |
| 18 | - |  | 8.52 | 265.6 |
| 19 | - |  | 8.56 | 232.8 |
| 20 | - |  | 8.64 | 242.9 |
| 21 | - |  | 8.98 | 217.4 |
| 22 | - |  | 9.27 | 238.5 |
| 23 | - |  | 9.61 | 212.1 |

| | | | | |
|----|---|--|------|-------|
| 24 | - | | 9.61 | 223.2 |
| 25 | - | | 9.66 | 265.6 |
| 26 | - | | 9.74 | 201.0 |
| 27 | - | | 10.3 | 160.0 |
| 28 | - | | 10.4 | 179.2 |
| 29 | - | | 10.6 | 188.8 |
| 30 | - | | 10.7 | 154.4 |
| 31 | - | | 10.8 | 226.3 |
| 32 | - | | 10.9 | 178.5 |
| 33 | - | | 10.9 | 190.9 |
| 34 | - | | 11.1 | 128.7 |
| 35 | - | | 11.1 | 156.7 |
| 36 | - | | 11.2 | 151.0 |
| 37 | - | | 11.2 | 257.3 |
| 38 | - | | 11.2 | 155.3 |
| 39 | - | | 11.3 | 111.6 |
| 40 | - | | 11.4 | 128.8 |
| 41 | - | | 11.5 | 149.0 |

| | | | | |
|----|---|--|------|-------|
| 42 | - |  | 11.5 | 135.3 |
| 43 | - |  | 11.6 | 114.2 |
| 44 | - |  | 11.7 | 154.4 |
| 45 | - |  | 11.7 | 168.4 |
| 46 | - |  | 11.8 | 134.4 |
| 47 | - |  | 11.8 | 146.0 |
| 48 | - |  | 11.9 | 105.4 |
| 49 | - |  | 12.0 | 105.7 |
| 50 | - |  | 12.0 | 157.0 |
| 51 | - |  | 12.0 | 169.1 |
| 52 | - |  | 12.0 | 181 |
| 53 | - |  | 12.0 | 126.0 |
| 54 | - |  | 12.0 | 109.4 |
| 55 | - |  | 12.0 | 148.9 |
| 56 | - |  | 12.1 | 197.0 |
| 57 | - |  | 12.1 | 125.6 |
| 58 | - |  | 12.2 | 110.0 |
| 59 | - |  | 12.3 | 133.1 |

| | | | | |
|----|---|--|------|-------|
| 60 | - | | 12.3 | 146.7 |
| 61 | - | | 12.4 | 132.5 |
| 62 | - | | 12.4 | 145.6 |
| 63 | - | | 12.7 | 102.7 |
| 64 | - | | 12.8 | 159.2 |
| 65 | - | | 12.8 | 155.0 |
| 66 | - | | 12.9 | 103.1 |
| 67 | - | | 12.9 | 98.3 |
| 68 | - | | 12.9 | 103.4 |
| 69 | - | | 13.0 | 103.6 |
| 70 | - | | 13.1 | 118.1 |
| 71 | - | | 13.1 | 176.8 |
| 72 | - | | 13.1 | 188.0 |
| 73 | - | | 13.3 | 126.1 |
| 74 | - | | 13.3 | 139.3 |
| 75 | - | | 13.5 | 157.3 |
| 76 | - | | 13.6 | 155.9 |
| 77 | - | | 13.8 | 95.6 |

| | | | | |
|----|---|---|------|-------|
| 78 | - |  | 13.9 | 96.4 |
| 79 | - |  | 14.1 | 193.8 |
| 80 | - |  | 14.4 | 150.3 |
| 81 | - |  | 14.5 | 175.4 |
| 82 | - |  | 14.8 | 89.1 |
| 83 | - |  | 15.2 | 129.0 |
| 84 | - |  | 15.6 | 129.0 |
| 85 | - |  | 15.6 | 152.6 |
| 86 | - |  | 15.6 | 165.5 |
| 87 | - |  | 15.8 | 149.2 |
| 88 | - |  | 16.4 | 126.5 |
| 89 | - |  | 16.4 | 126.5 |
| 90 | - |  | 16.4 | 174.0 |
| 91 | - |  | 17.3 | 119.2 |

2.2 Characterization of PCs

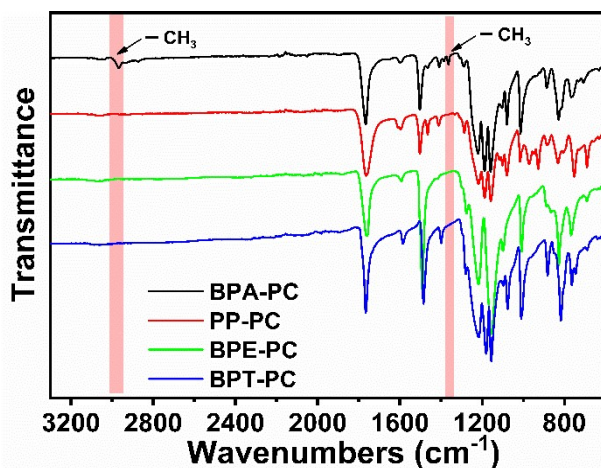


Figure S4. FI-IR spectra of PPA-PC, PP-PC, BPE-PC and BPT-PC.

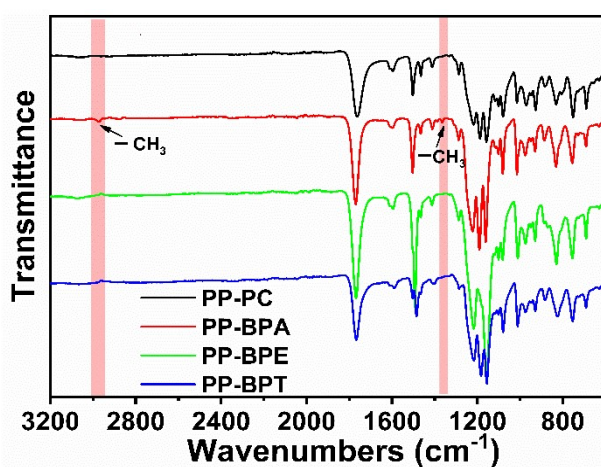


Figure S5. FI-IR spectra of PP-PC, PP-BPA, PP-BPE and PP-BPT.

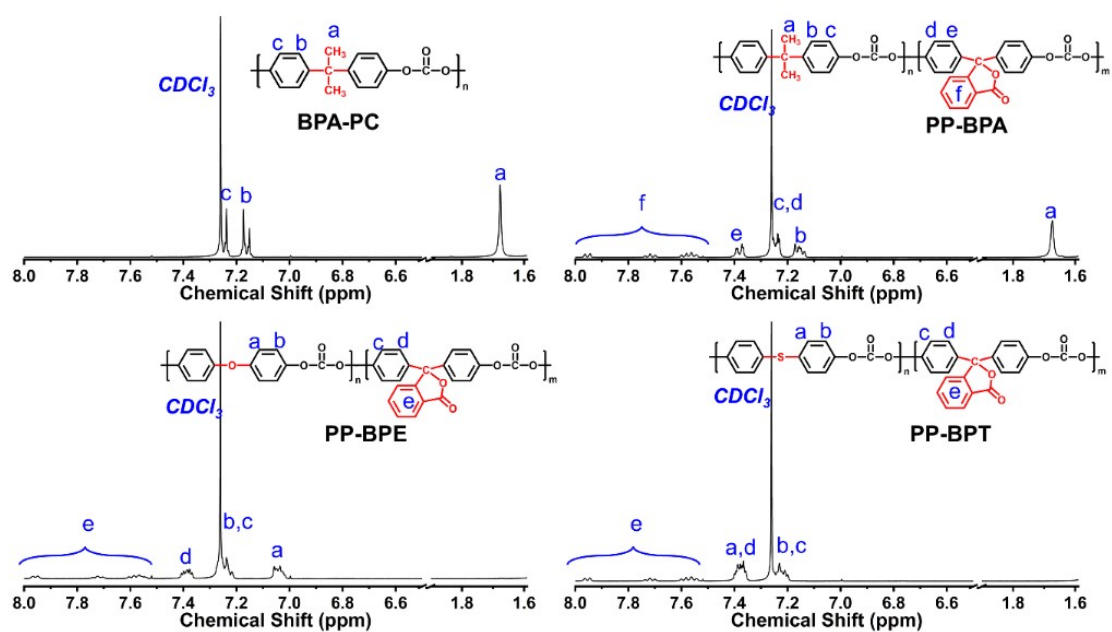


Figure S6. ¹H NMR spectra of BPA-PC, PP-BPE, PP-BPT and PP-BPT.

Table S3 The number-average molecular weight of PCs

| Sample | PP content (mol%) | | M_n |
|--------|-------------------|-------------------|-------|
| | Cal. | Exp. ^a | |
| BPA-PC | - | - | 14611 |
| PP-BPA | 50 | 48 | 13176 |
| PP-BPE | 50 | 47 | 16496 |
| PP-BPT | 50 | 49 | 16220 |

^a The results were obtained from ¹H NMR spectra.

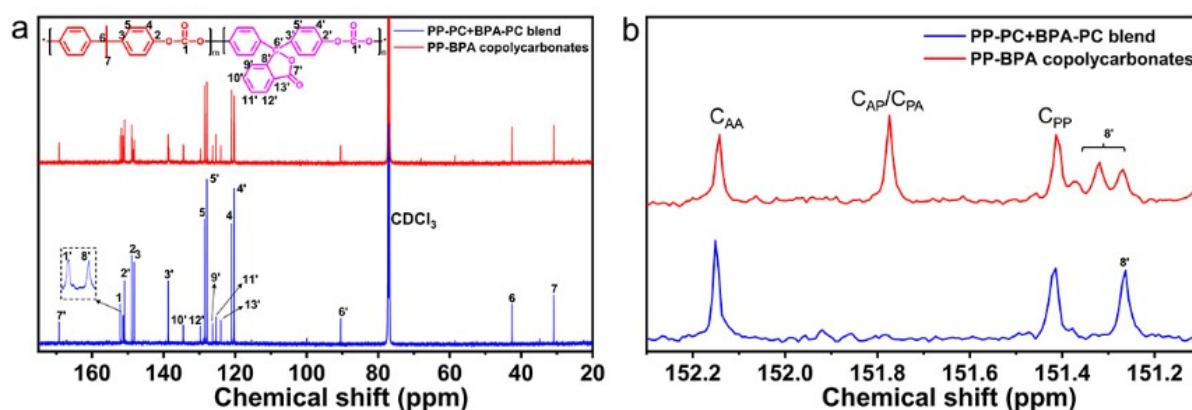


Figure S7. (a) ¹³C NMR spectra of PP-BPA (co-PC) and BPA-PC/PP-PC blend. (b) Detailed C1 and C1' ¹³C NMR spectra of PP-BPA (co-PC) and BPA-PC/PP-PC blend

Table S4 Units of linkages in the PP-BPA chain and chemical shifts of carbon atoms

| Type | Units of linkages in copolymer chain | Chemical shifts (δ)/ppm |
|---------|--------------------------------------|----------------------------------|
| PCP | | $C_{PP}=151.41$ |
| ACP/PCA | | $C_{PA}=C_{AP}=151.77$ |
| ACA | | $C_{AA}=152.14$ |

For polymer blends, there should be only two chemical shifts of carbon atoms in O-CO-O structure. However, three types of linking units in PP-BPA are observed. So, the ^{13}C NMR results (Figure S7, Table S4) proved the copolymerized structure of PP-BPA.

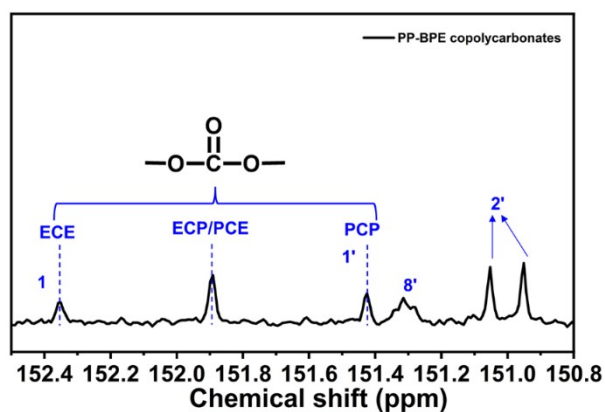


Figure S8. Detailed C1 and C1' ^{13}C NMR spectra of PP-BPE (co-PC).

Table S5 Units of linkages in the PP-BPE chain and chemical shifts of carbon atoms

| Type | Units of linkages in copolymer chain | Chemical shifts (δ)/ppm |
|---------|--------------------------------------|----------------------------------|
| PCP | | $C_{PP}=151.43$ |
| ECP/PCE | | $C_{PE}=C_{EP}=151.89$ |
| ECE | | $C_{EE}=152.35$ |

The ^{13}C NMR results (Figure S8, Table S5) proved the copolymerized structure of PP-BPE.

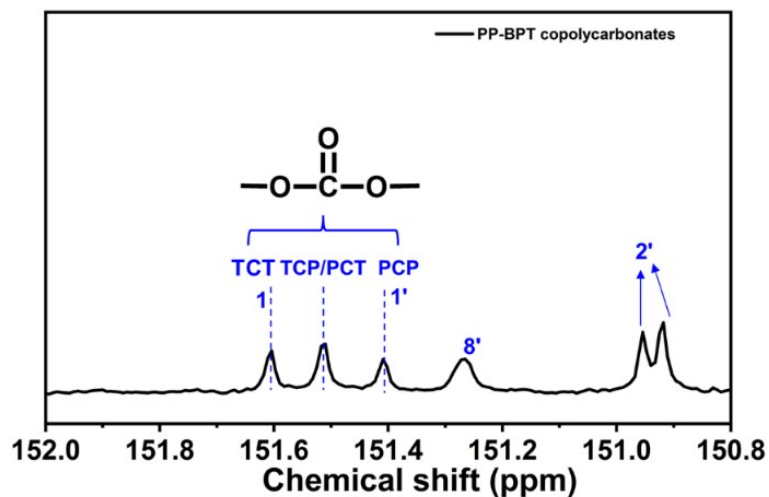


Figure S9. Detailed C1 and C1' ^{13}C NMR spectra of PP-BPT (co-PC).

Table S6 Units of linkages in the PP-BPT chain and chemical shifts of carbon atoms

| Type | Units of linkages in copolymer chain | Chemical shifts (δ)/ppm |
|---------|--------------------------------------|----------------------------------|
| PCP | | $C_{PP}=151.41$ |
| TCP/PCT | | $C_{PT}=C_{PT}=151.51$ |
| TCT | | $C_{TT}=151.61$ |

The ^{13}C NMR results (Figure S9, Table S6) proved the copolymerized structure of PP-BPT.

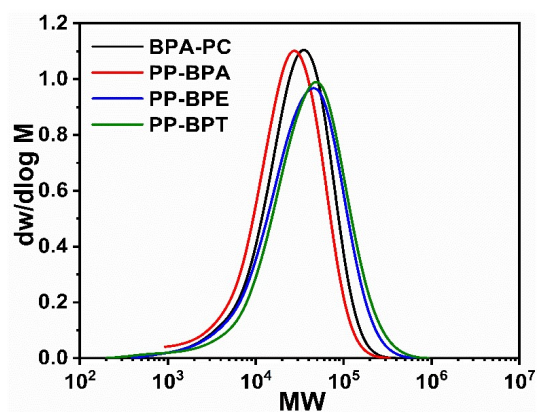


Figure S10. GPC curves of BPA-PC and co-PCs with different chemical structure in THF.

2.3 DSC and TGA analysis

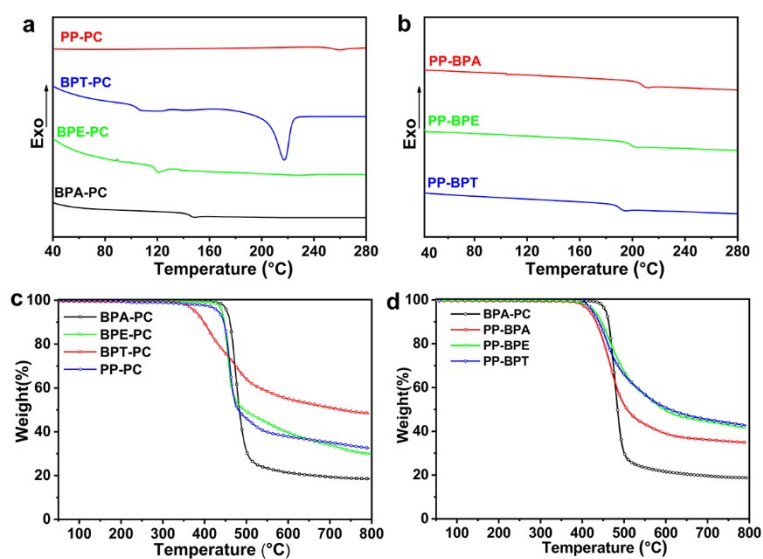


Figure S11. (a-b) DSC and (c-d) TGA curves of BPA-PC and co-PCs with different chemical structure in nitrogen.

2.4 PCFC analysis

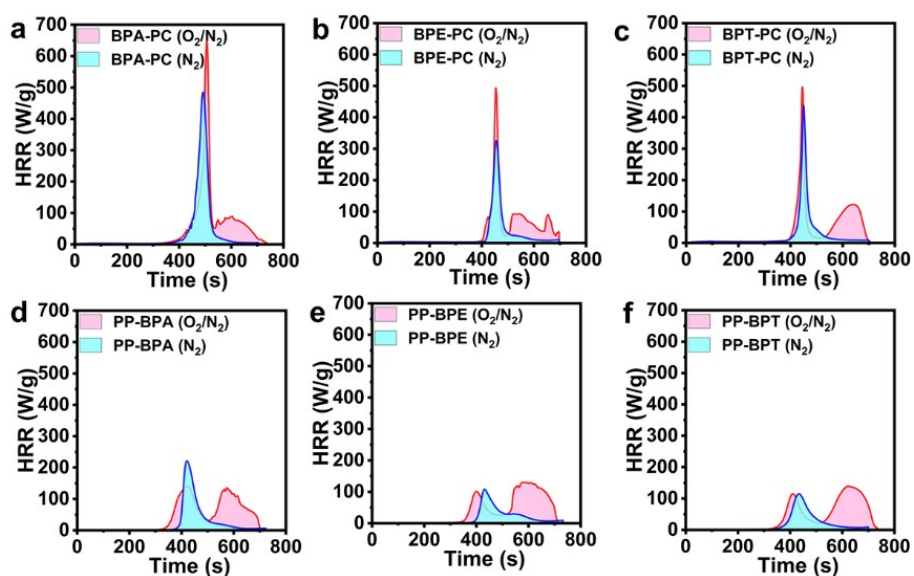


Figure S12. (a-f) Heat release rate (HRR) curve of BPA-PC and co-PCs with different chemical structure, obtained from PCFC test in N_2 and O_2/N_2 .

Table S7 Comparison for the optimized co-PCs and other polymers

| Sample | CAS | $h_{c,exp}^a$ | $T_{g,exp}^b$ |
|--------|------------|---------------|---------------|
| PMMA | 9011-14-7 | 24.3 | 105 |
| BPA-PC | 25037-45-0 | 21.9 | 148 |
| PSU | 25135-51-7 | 17.7 | 190 |
| PAR | 25212-77-5 | 19.4 | 184 |
| PPSU | 25839-81-0 | 11.3 | 220 |
| PES | 25667-42-9 | 11.2 | 225 |
| PEI | 61128-46-9 | 11.8 | 250 |
| PAI | 42955-03-3 | 6.6 | 285 |
| PI | 26023-21-2 | 7.1 | 333 |
| PP-BPA | - | 13.9 | 209 |
| PP-BPE | - | 8.6 | 199 |
| PP-BPT | - | 9.3 | 191 |

^aThe $h_{c,exp}$ values were obtained in this report [3];

^bThe $T_{g,exp}$ values were obtained in the SciFinder and ChemSpider databases.

2.5 Fire-safe performance

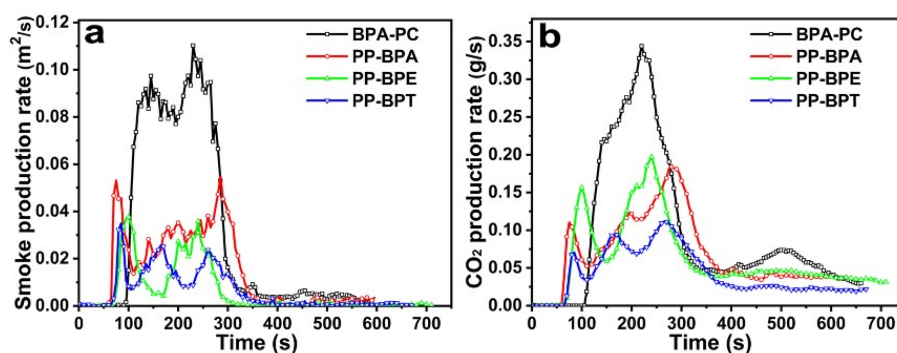


Figure S13. The results obtained from cone calorimeter test for BPA-PC and co-PCs with different chemical structure. (a) Smoke production rate (SPR) curves. (b) CO_2 production rate (CO_2P) curves.

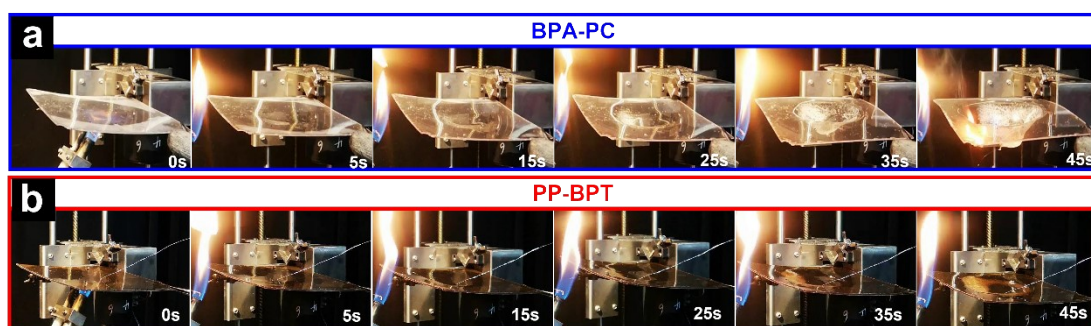


Figure S14. Photographs for UL 94 5V testing using strip samples: (a) BPA-PC and (b) PP-BPT.



Figure S15. Digital photographs of char residue after strip sample testing for BPA-PC and PP-BPT.

2.6 Transparency of PCs

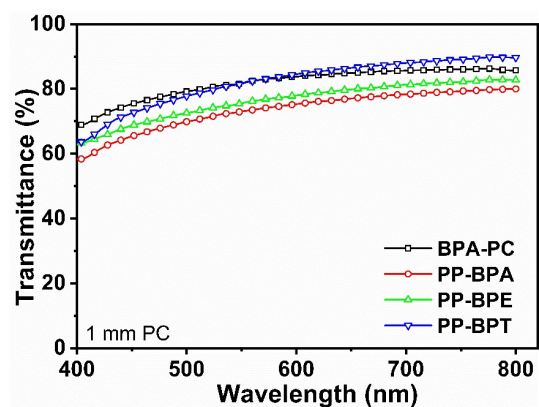


Figure S16. UV–Vis spectra from the wavelength of 400 to 800 nm for BPA-PC and co-PCs with different chemical structure.

2.7 Morphology and microstructure of residual chars

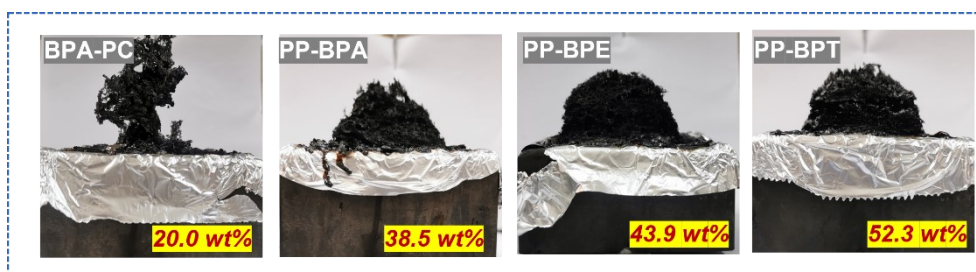


Figure S17. Top-view photographs of the residual char after cone calorimeter test for BPA-PC and co-PCs with different chemical structure.

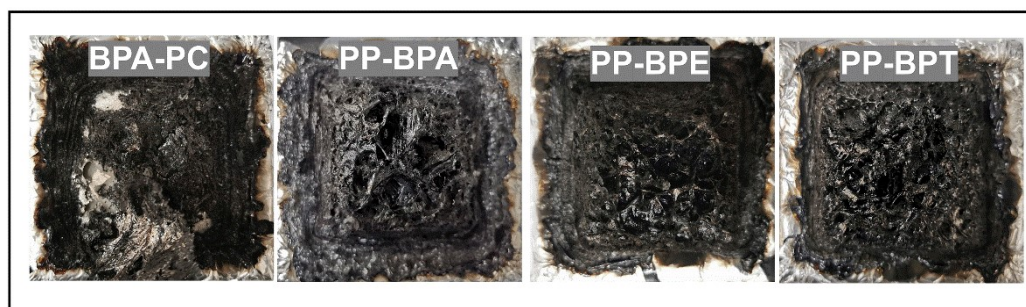


Figure S18. Top-view photographs of the residual char after cone calorimeter test for BPA-PC and co-PCs with different chemical structure.

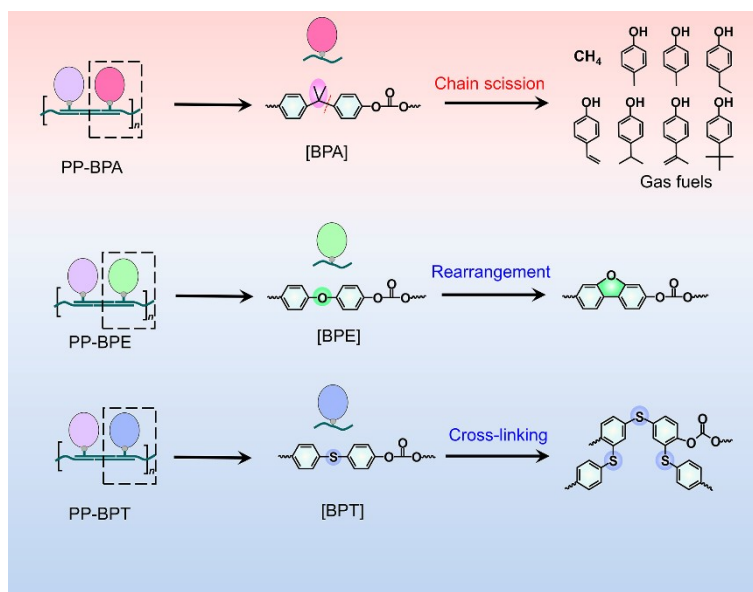


Figure S19. Possible chain scission of BPA structural unit from PP-BPA, possible rearrangement of BPE structural unit from PP-BPE and the crosslinking behavior of BPT structural unit from PP-BPT.

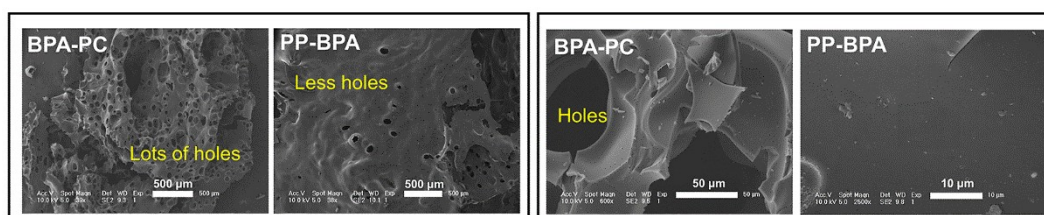


Figure S20. The SEM images of the external residual char for BPA-PC and PP-BPA.

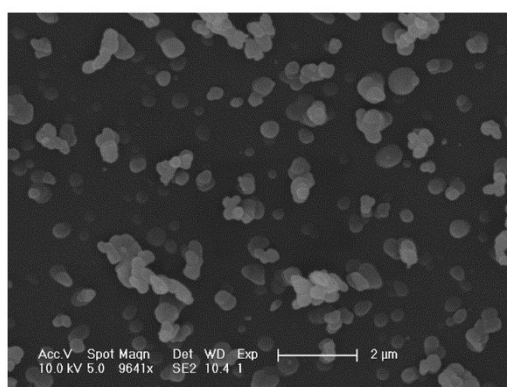


Figure S21. High-resolution SEM image for the particle morphology on the surface of external residual char from PP-BPT.

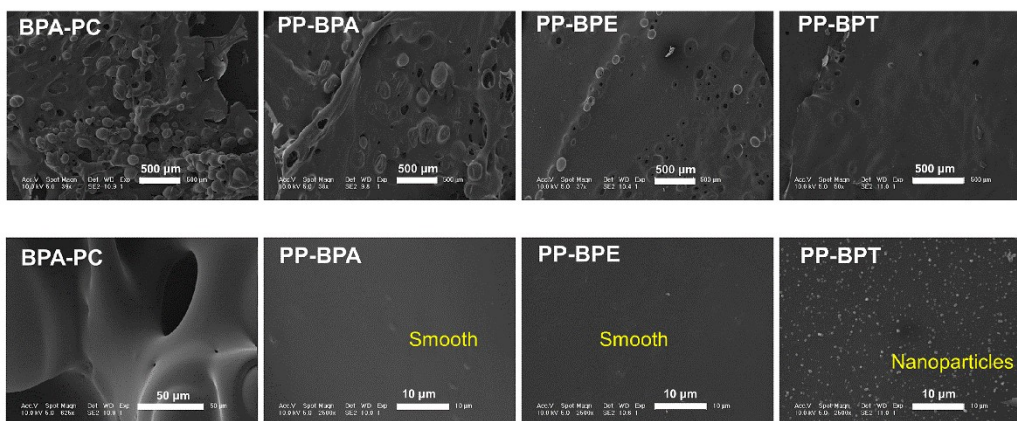


Figure S22. The SEM images of the internal residual char for BPA-PC and co-PCs with different chemical structure.

2.8 Pyrolysis analysis

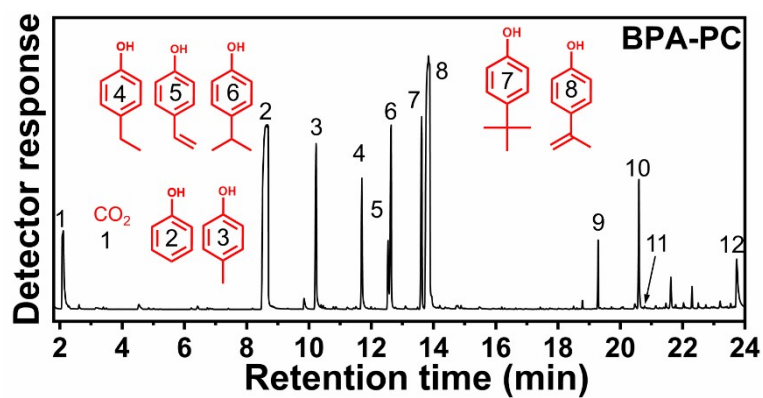


Figure S23. Chromatogram profile of BPA-PC obtained from Py-GC-MS test.

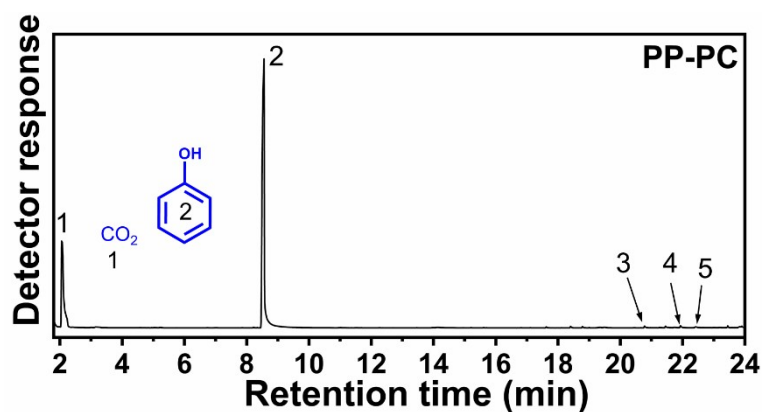


Figure S24. Chromatogram profile of PP-PC obtained from Py-GC-MS test.

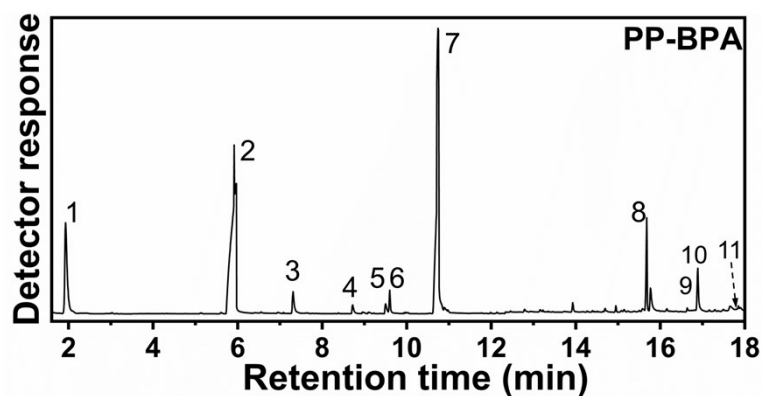


Figure S25. Chromatogram profile of PP-BPA obtained from Py-GC-MS test.

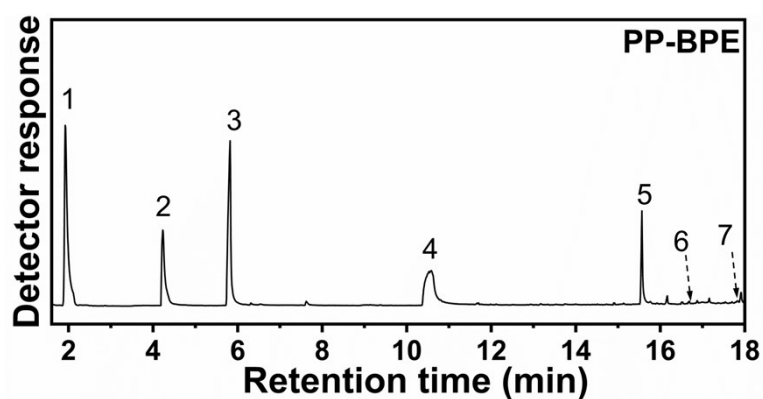


Figure S26. Chromatogram profile of PP-BPE obtained from Py-GC-MS test.

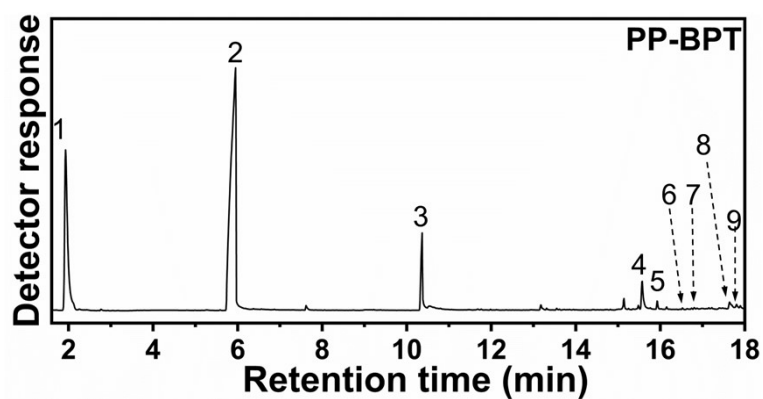
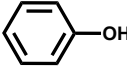
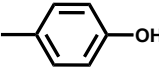

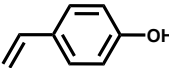

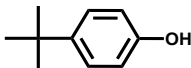
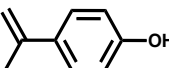
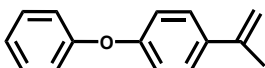
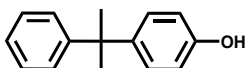
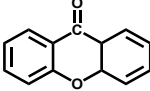
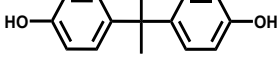
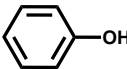
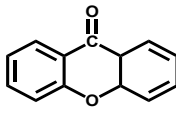
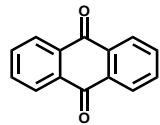
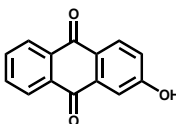
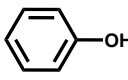
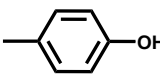
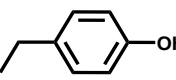
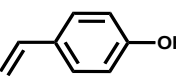
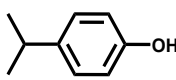
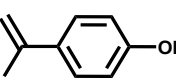
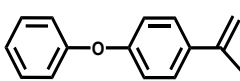
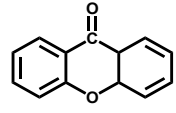
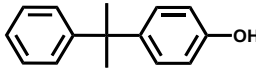
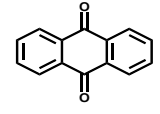
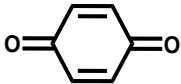
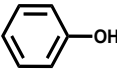

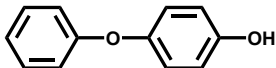
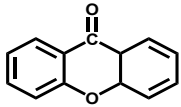
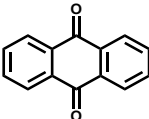
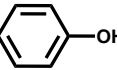
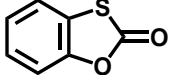
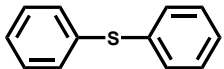
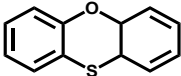
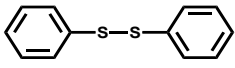
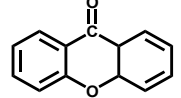
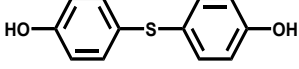
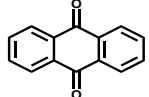


Figure S27. Chromatogram profile of PP-BPT obtained from Py-GC-MS test.

Table S8. Compounds detected by the Py-GC-MS test from the decomposition of BPA-PC, PP-PC and co-PCs with different chemical structure at 550°C

| Sample | Peak# | Retention time | M | Compound | Major mass fragments |
|--------|-------|----------------|-----|--|----------------------|
| BPA-PC | 1 | 2.11 | 44 | CO ₂ | 44 |
| | 2 | 8.63 | 94 |  | 94, 66 |
| | 3 | 10.32 | 107 |  | 107, 90, 77 |
| | 4 | 11.69 | 122 |  | 122, 107 |
| | 5 | 12.52 | 120 |  | 91, 120 |
| | 6 | 12.66 | 136 |  | 121, 136 |
| | 7 | 13.59 | 150 |  | 135, 150 |
| | 8 | 13.86 | 134 |  | 119, 134 |
| | 9 | 19.33 | 210 |  | 195, 210 |
| | 10 | 20.60 | 212 |  | 197, 212 |
| | 11 | 20.80 | 196 |  | 168, 196 |
| | 12 | 23.47 | 228 |  | 119, 213, 228 |
| PP-PC | 1 | 2.09 | 44 | CO ₂ | 44 |
| | 2 | 8.58 | 94 |  | 94, 66 |

| | | | | | |
|--------|----|-------|-----|--|---------------|
| | 3 | 20.79 | 196 |  | 168, 196 |
| | 4 | 21.99 | 208 |  | 152, 180, 208 |
| | 5 | 22.42 | 224 |  | 168, 224 |
| | 1 | 1.92 | 44 | CO ₂ | 44 |
| | 2 | 5.96 | 94 |  | 94, 66 |
| | 3 | 7.31 | 107 |  | 107, 90, 77 |
| | 4 | 8.72 | 122 |  | 122, 107 |
| | 5 | 9.49 | 120 |  | 91, 120 |
| PP-BPA | 6 | 9.62 | 136 |  | 121, 136 |
| | 7 | 10.76 | 134 |  | 119, 134 |
| | 8 | 15.67 | 210 |  | 195, 210 |
| | 9 | 16.82 | 196 |  | 168, 196 |
| | 10 | 16.87 | 212 |  | 197, 212 |
| | 11 | 17.78 | 208 |  | 152, 180, 208 |
| PP-BPE | 1 | 1.92 | 44 | CO ₂ | 44 |

| | | | | | |
|--------|---|-------|-----|--|------------------|
| | 2 | 4.25 | 108 |  | 82, 108 |
| | 3 | 5.79 | 94 |  | 94, 66 |
| | 4 | 10.58 | 110 |  | 81, 110 |
| | 5 | 15.58 | 186 |  | 157, 186 |
| | 6 | 16.84 | 196 |  | 168, 196 |
| | 7 | 17.82 | 208 |  | 152, 180, 208 |
| | 1 | 1.92 | 44 | CO ₂ | 44 |
| | 2 | 5.97 | 94 |  | 94, 66 |
| | 3 | 10.36 | 152 |  | 152 |
| | 4 | 15.63 | 186 |  | 186 |
| PP-BPT | 5 | 15.92 | 200 |  | 168, 200 |
| | 6 | 16.53 | 218 |  | 185, 218 |
| | 7 | 16.81 | 196 |  | 168, 196 |
| | 8 | 17.43 | 218 |  | 186, 218 |
| | 9 | 17.83 | 208 |  | 152, 180, 208 |

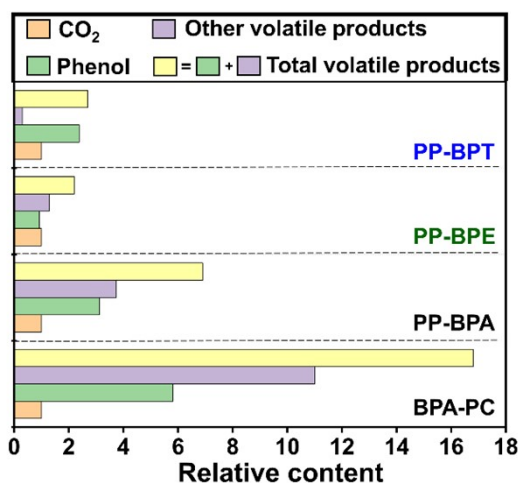


Figure S28. Relative peak area of low molecular weight pyrolysis products of PC in the gas chromatogram.

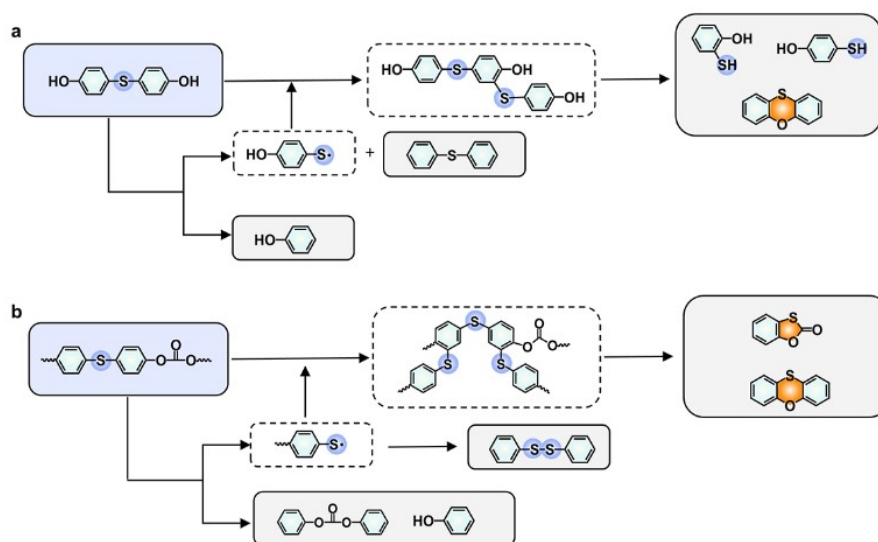


Figure S29. (a) Possible pyrolysis processes of BPT structural unit. (b) Possible pyrolysis processes of BPT-PC.

3. References

- [1] D. W. Van Krevelen and K. Te Nijenhuis, Properties of polymers: their correlation with chemical structure; their numerical estimation and prediction from additive group contributions. Elsevier. 2009.
- [2] R. E. Lyon, Fire Mater, 2000, **24**, 179-186.
- [3] R. N. Walters and R. E. Lyon, J. Appl. Polym. Sci., 2003, **87**, 548-563.
- [4] R. E. Lyon, M. T. Takemori, N. Safronava, S. I. Stoliarov and R. N. Walters, Polymer, 2009, **50**, 2608-2617.