Supporting information for

The copolymerization reactivity of diols with 2,5-furandicarboxylic acid for furan-based copolyester materials

Jiping Ma,[abc] Yi Pang,*[a] Min Wang,[bc] Jie Xu,*[b] Hong Ma,[b] and Xin Nie[b]

[a] *Department of Chemistry, The University of Akron, Akron, OH, 44325, USA*

E-mail: yp5@uakron.edu

[b] *Dalian National Lab for Clean Energy, State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, P. R. China*

Fax: (+86)-411-84379245; E-mail: xujie@dicp.ac.cn

[c] *Graduate University of the Chinese Academy of Sciences, Beijing 100039, P. R. China*

Table of Contents:

1. Synthesis of 2,5-furandicarboxylic acid (FDCA).

Chemicals

NaOH was purchased from Aldrich. $KMnO_4$ was from Acros Organics. HCl (37%) was purchased from Mallinckrodt Baker, Inc. All reagents were of analytical grade unless otherwise mentioned and used as received.

Procedure

DFF (1.99 g, 16.07 mmol) and 50 mL H_2O was placed in a 250 mL round-bottom flask equipped with a magnetic stirrer. A solution of $KMnO_4$ (3.90 g, 24.65 mmol) in 50 mL of 10% aq. NaOH was added dropwise with stirring over a period of 0.5 h. Then, the mixture was allowed to stir for an additional 1 h at room temperature, and the resulting precipitate was removed by filtration. The filtrate was treated with a 37% HCl solution until PH = 1 or less. A pale yellow solid (1.95 g, 78%) was isolated by suction filtration, washed with water, and dried. ^{1}H NMR (300 MHz, DMSO-d_6, 298K): 13.63 (2H, s, -COOH), 7.29 (2H, s, furan-H); ^{13}C NMR: 158.92 (-COOH), 147.07 (C2/C5), 118.40 (C3/C4). FT-IR (KBr, ν_{max}/cm^{-1}): 3152 and 3126 (C-H); 1693 (C=O); 1573 (C=C); 1423 and 1275 (furan C-O-C); 1040, ring breathing; 961, 851, and 763 bending motions associated with the 2,5-disubstituted furan ring.

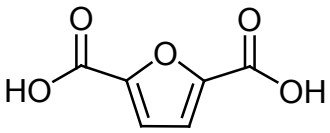

Figure S1. ^{1}H NMR (DMSO-d_6) of 2,5-furandicarboxylic acid.

Figure S2. ^{13}C NMR (DMSO-d_6) of 2,5-furandicarboxylic acid.

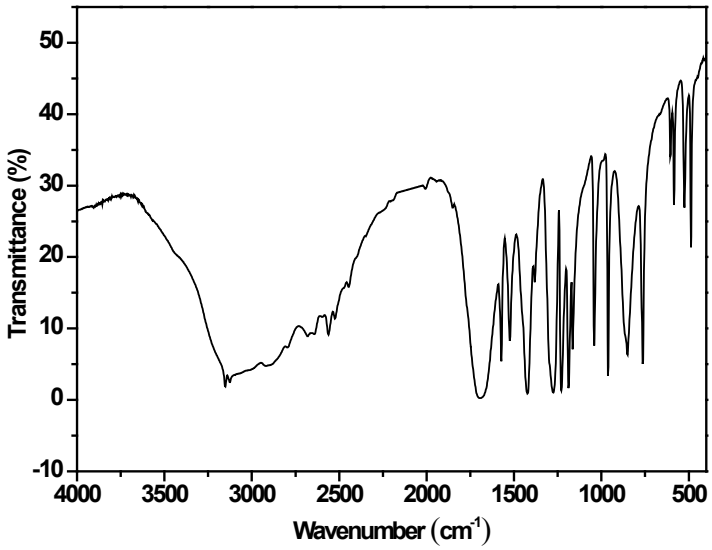

Figure S3. FT-IR (KBr) of 2,5-furandicarboxylic acid.

2. Intrinsic viscosity determination

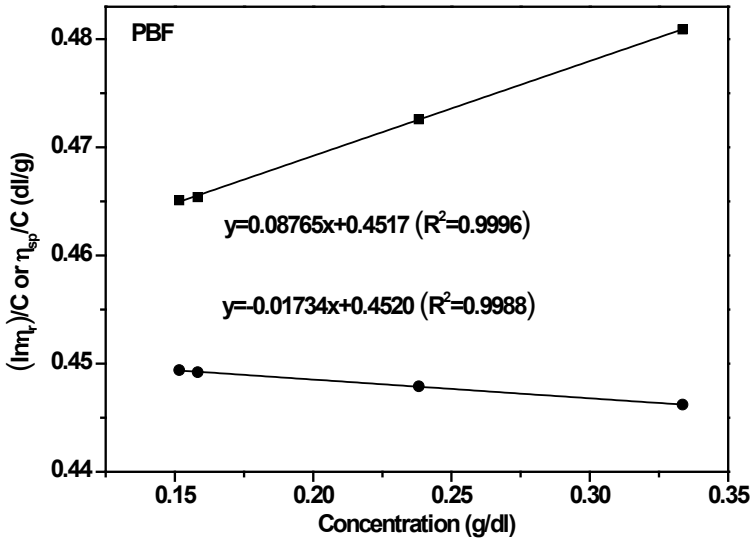

Figure S4. η_{sp}/C (■) or $(In\eta_r)/C$ (●) of PBF versus concentration.

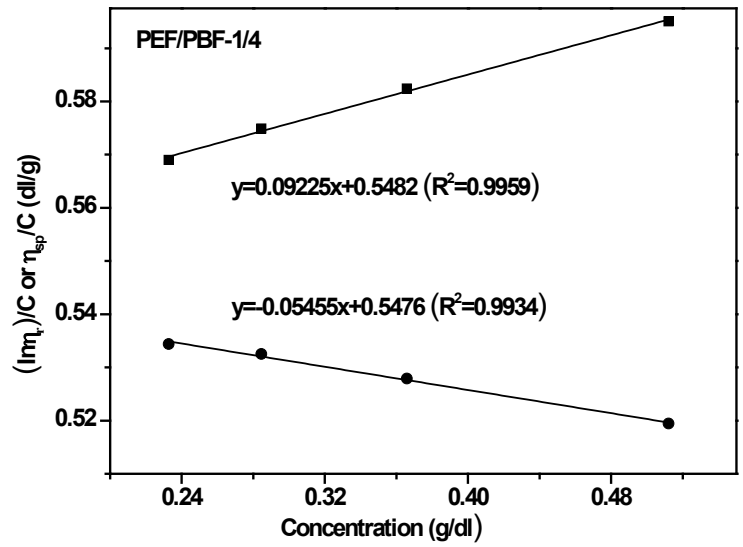

Figure S5. η_{sp}/C (■) or $(In\eta_r)/C$ (●) of PEF/PBF-1/4 versus concentration.

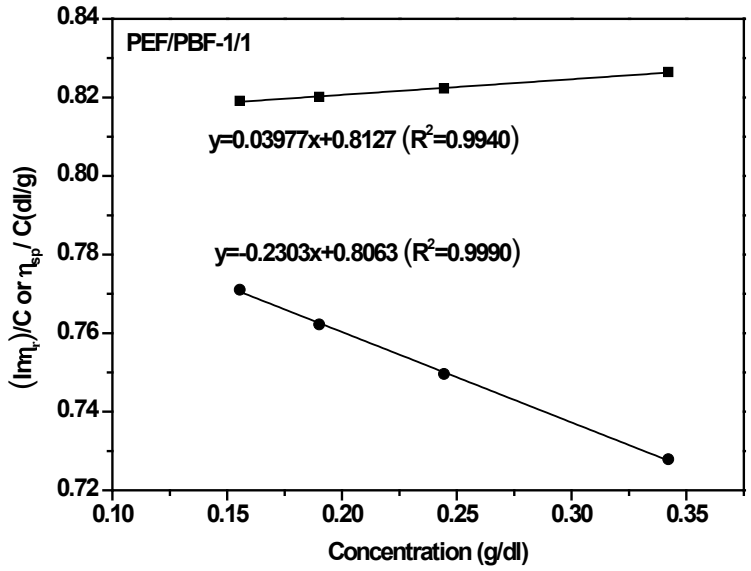

Figure S6. η_{sp}/C (■) or $(In\eta_r)/C$ (●) of PEF/PBF-1/1 versus concentration.

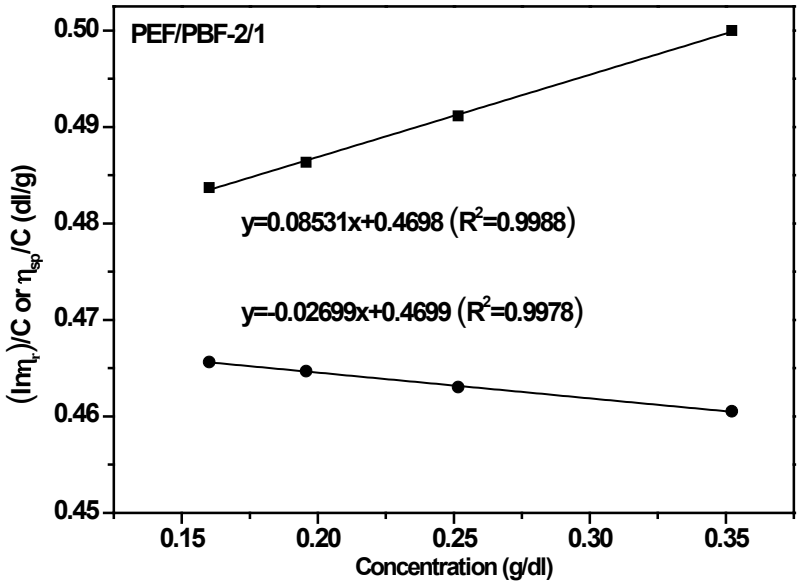

Figure S7. η_{sp}/C (■) or $(In\eta_r)/C$ (●) of PEF/PBF-2/1 versus concentration.

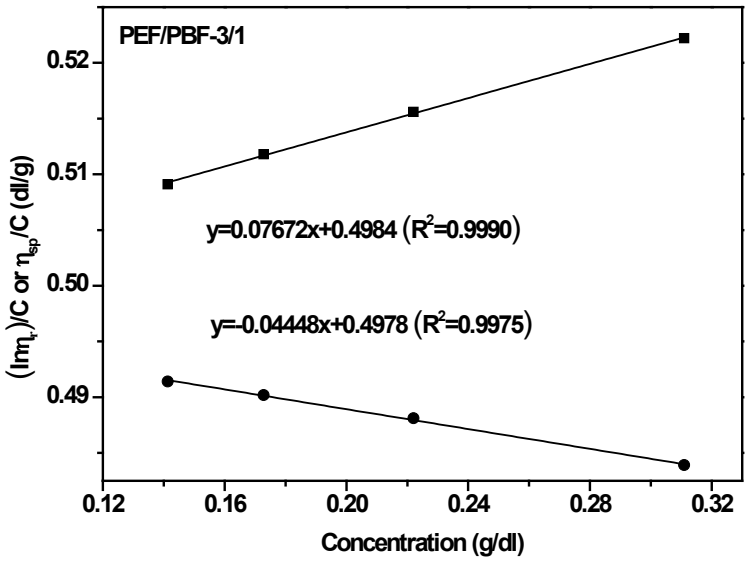

Figure S8. η_{sp}/C (■) or $(In\eta_r)/C$ (●) of PEF/PBF-3/1 versus concentration.

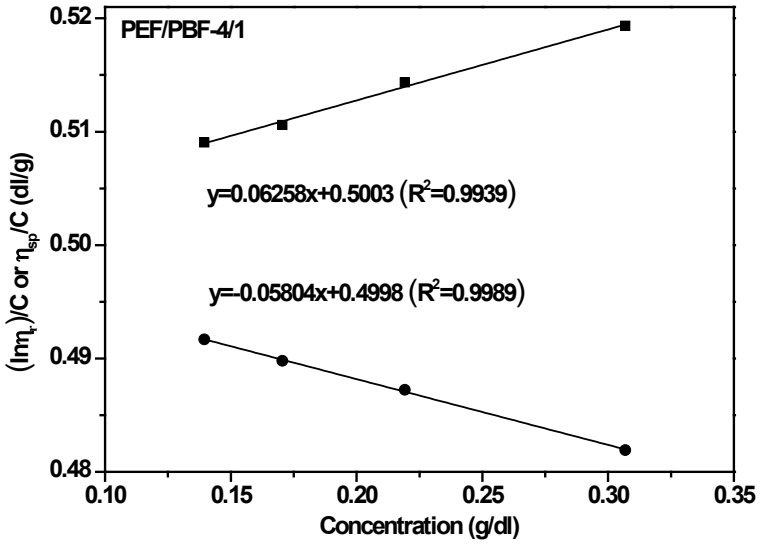

Figure S9. η_{sp}/C (■) or $(In\eta_r)/C$ (●) of PEF/PBF-4/1 versus concentration.

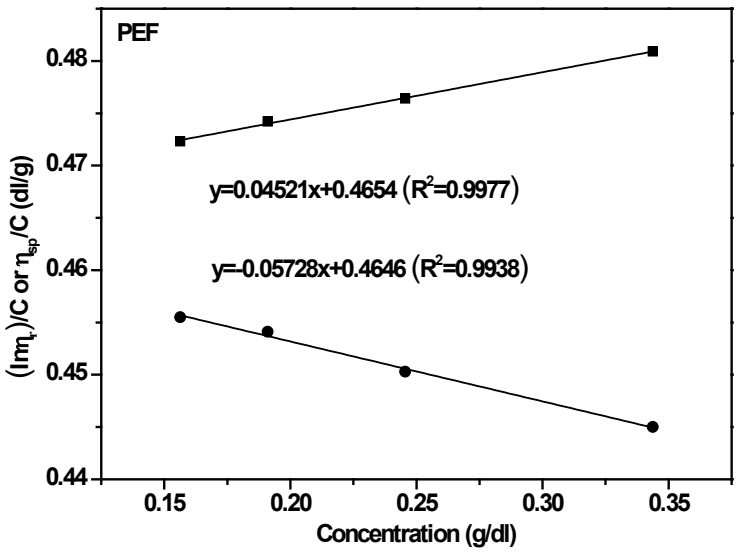

Figure S10. η_{sp}/C (■) or $(In\eta_r)/C$ (●) of PEF versus concentration.

3. Reactivity of diols reaction with FDCA determination

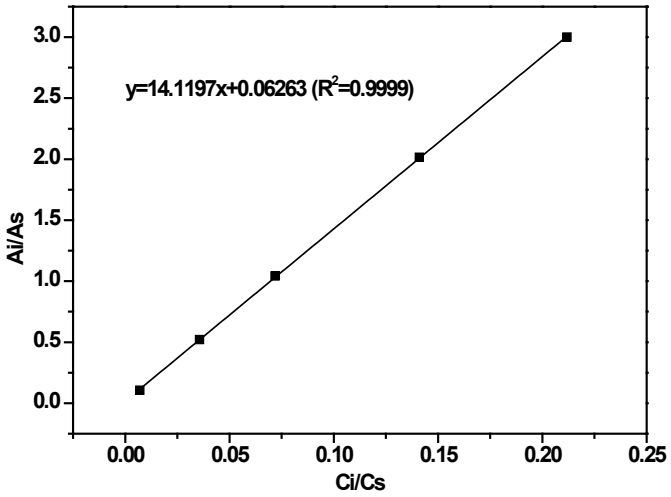

Figure S11. Standard line of FDCA using malonic acid as internal standard.

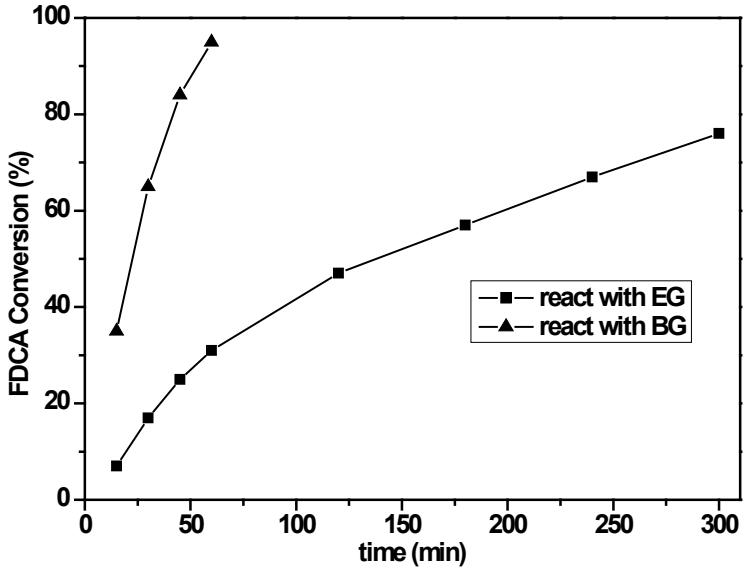

Figure S12. Plot of FDCA conversion as a function of reaction time.

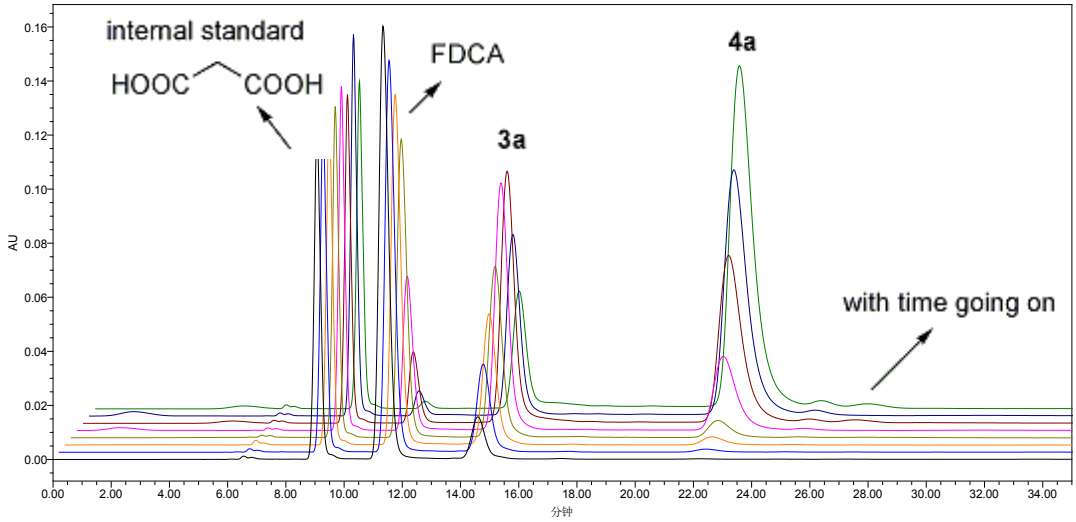

Figure S13. Changes of HPLC spectra of FDCA reaction with EG as a function of reaction time (The first samples were taken after 15 min, and then at 15-min intervals for 60 min, and then at 1-h intervals for 5 h).

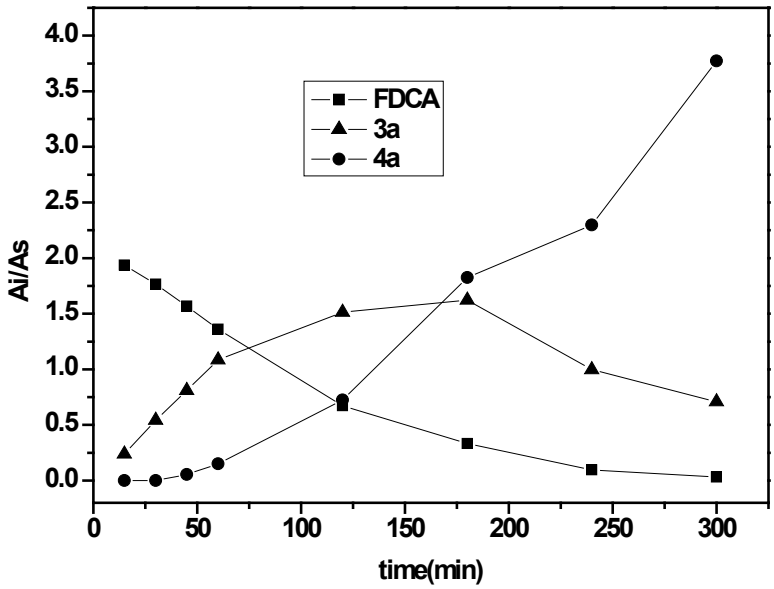

Figure S14. Plot of area ratio of FDCA, **3a** and **4a** to that of internal standard as a function of reaction time.

ESI-MS: Q-TOF Premier MS (Waters Corporation) using the ESI emitters. The MS was operated in positive V-mode with typical resolving power of at least 8000. The MS detector was calibrated from *m*/*z* 50 to 1000 by the MS/MS fragment ions of GFP. The radio frequency (RF) offset applied to the quadrupole mass analyzer was adjusted in order that the LC/MS data were effectively acquired from *m*/*z* 50 to 1000. The spectrum integration time was 0.9 s for MS scan (*m*/*z* 50–1000) and 1.2 s for MS/MS scan (*m*/*z* 50–1000) with an inter-scan delay time of 0.05 s.

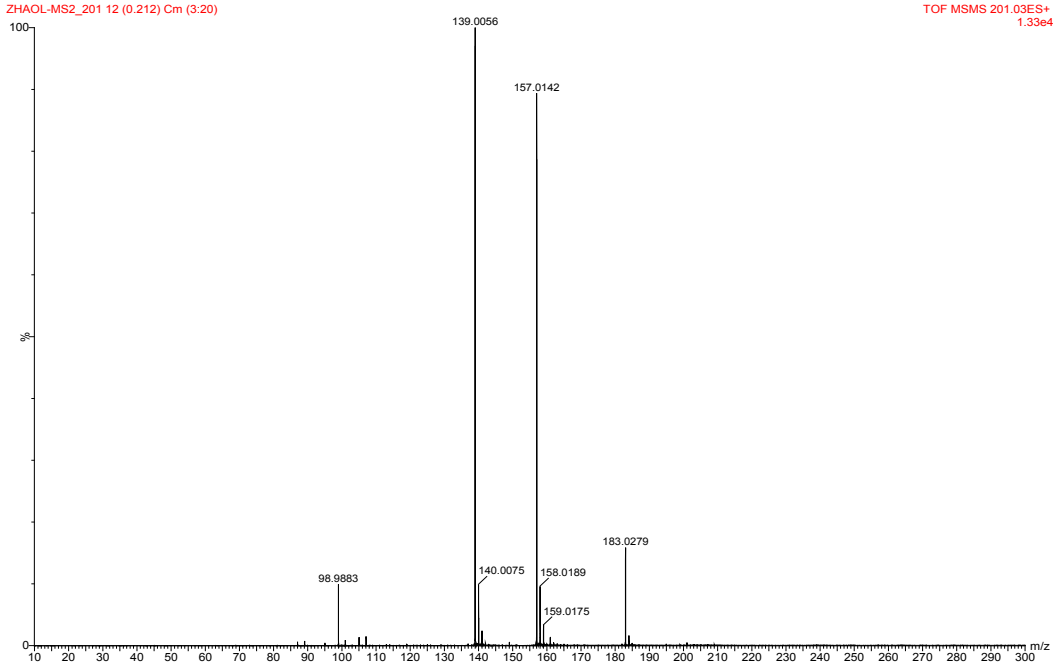

Figure S15. ESI-MS spectrum of **3a**.

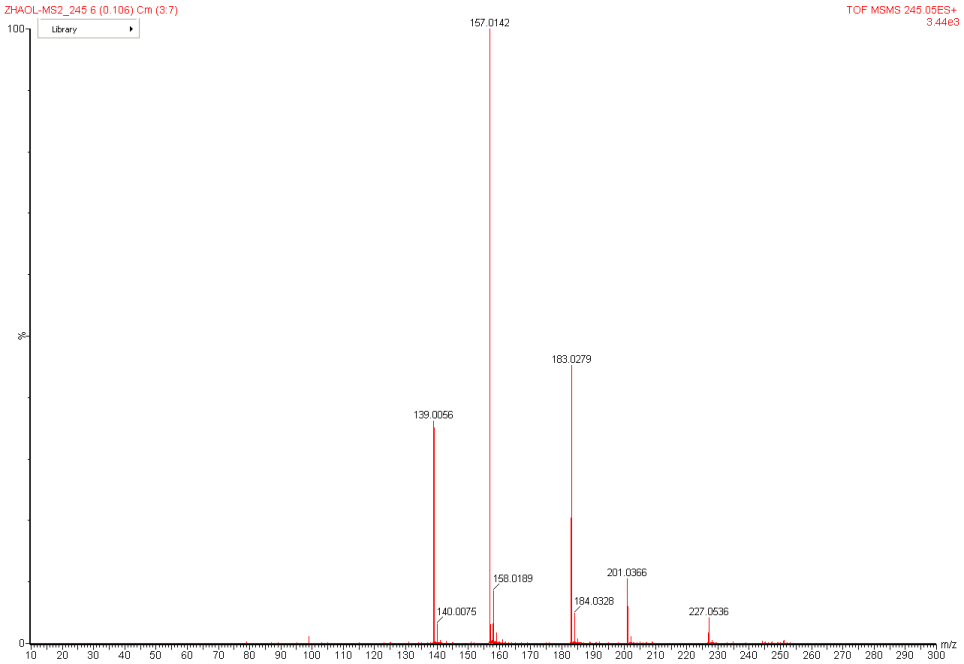

Figure S16. ESI-MS spectrum of **4a**.

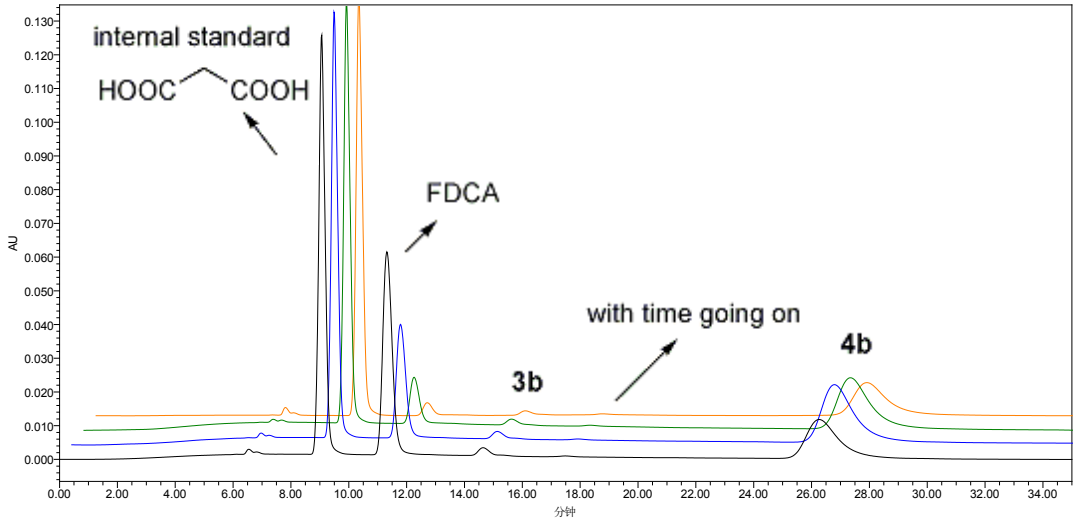

Figure S17. Changes of HPLC spectra of FDCA reaction with BG as a function of reaction time (The first samples were taken after 15 min, and then at 15-min intervals for 60 min).

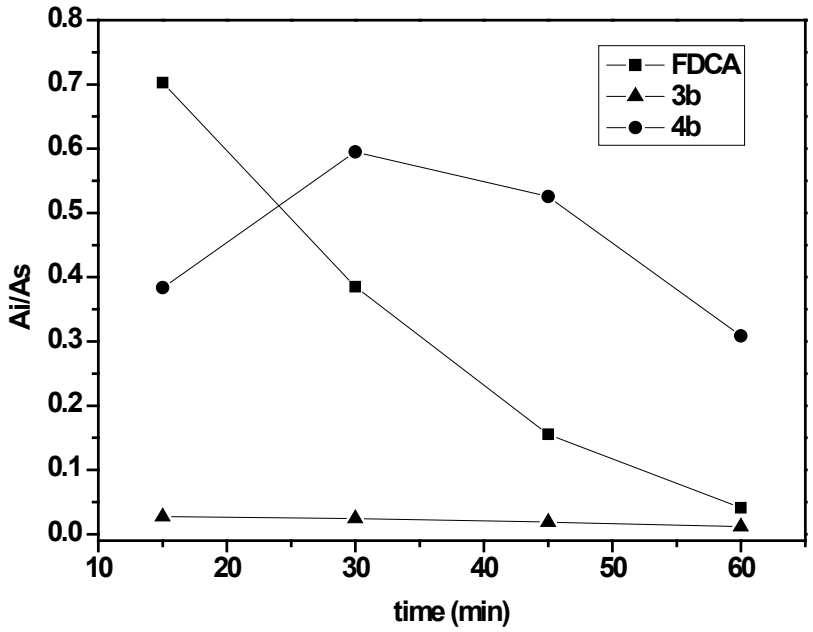

Figure S18. Plot of area ratio of FDCA, **3b** and **4b** to that of internal standard as a function of reaction time.

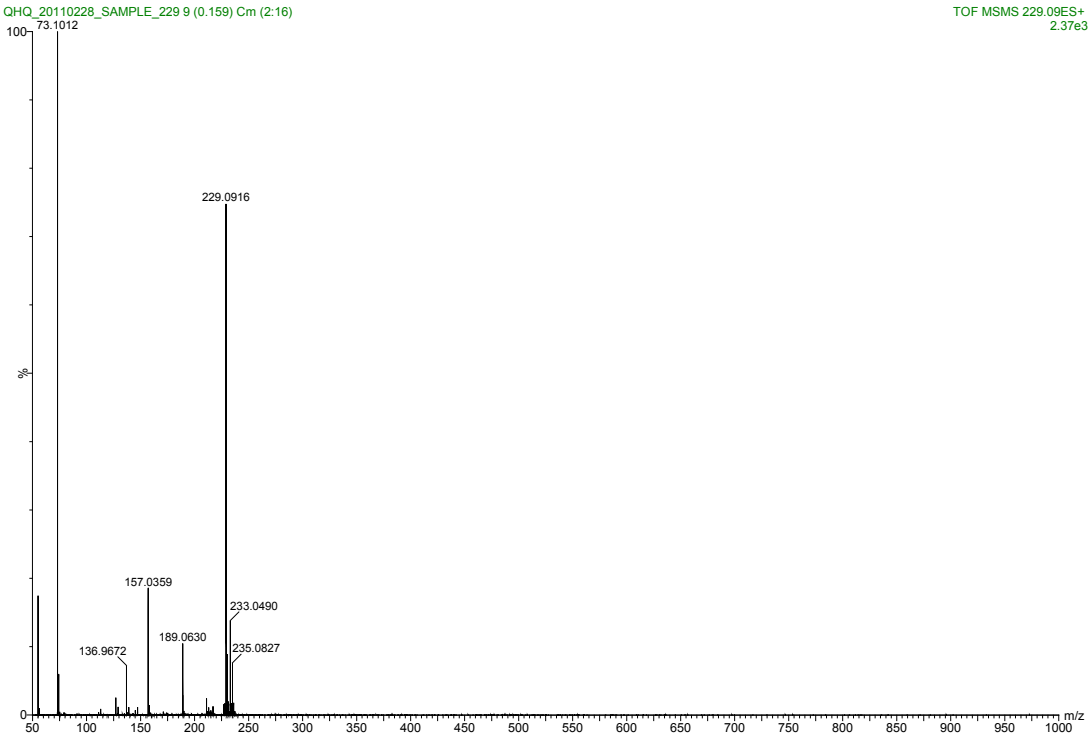

Figure S19. ESI-MS spectrum of **3b**.

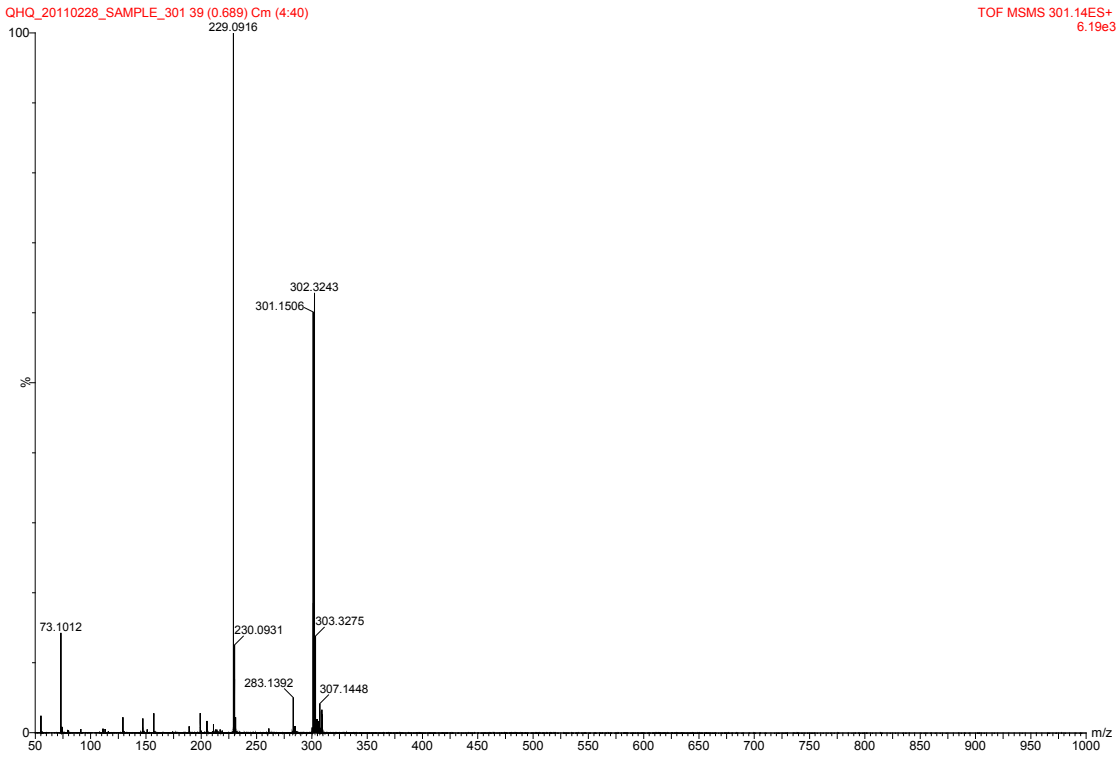

Figure S20. ESI-MS spectrum of **4b**.

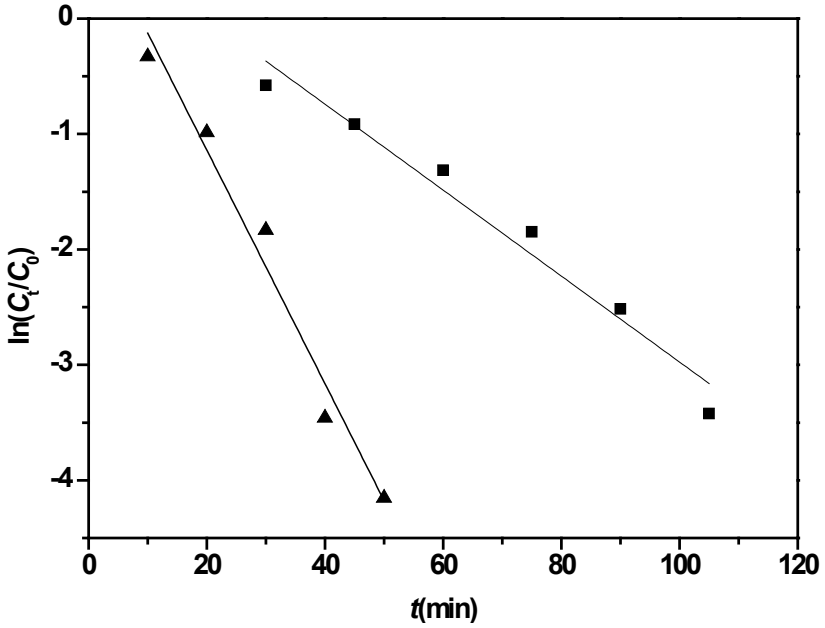

Figure S21. Relationship of $\ln(C_t/C_0)$ and reaction time t of FDCA reacting with 1,3-trimethylene glycol (■) and 1,5-pentylene glycol (▲), respectively. C_t and C_0 represent the concentration of FDCA at time t and at the beginning of the reaction, respectively.

4. Thermal properties determination

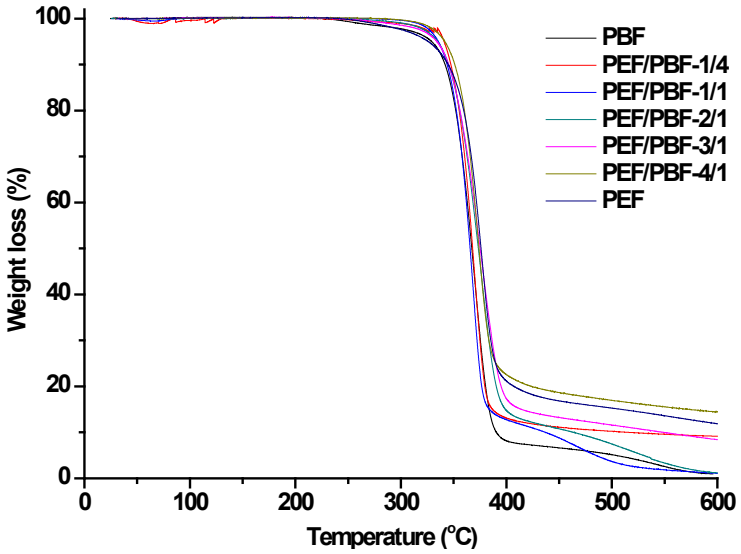

Figure S22. Thermogravimetric curves of as-prepared copolyesters. Conditions: sample was heated at a rate of 10 °C/min under nitrogen flow (25 mL/min).

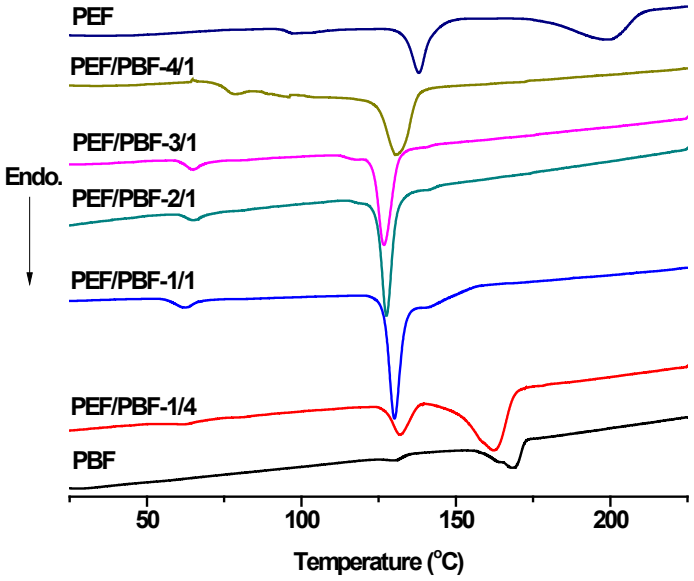

Figure S23. The first DSC heating traces of the as-prepared copolyesters. Conditions: the sample was heated at a rate of 40 °C/min under nitrogen flow (25 mL/min).

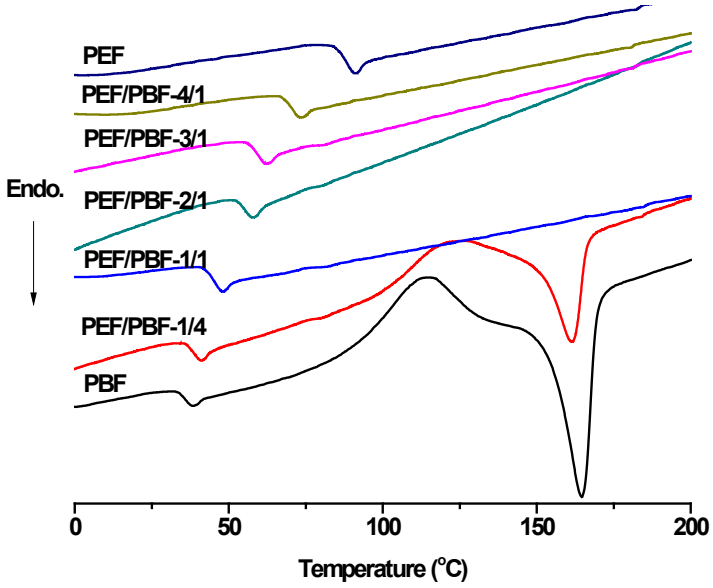

Figure S24. The second DSC heating traces of the as-prepared copolyesters. Conditions: the sample was heated at a rate of 40 °C/min under nitrogen flow (25 mL/min).

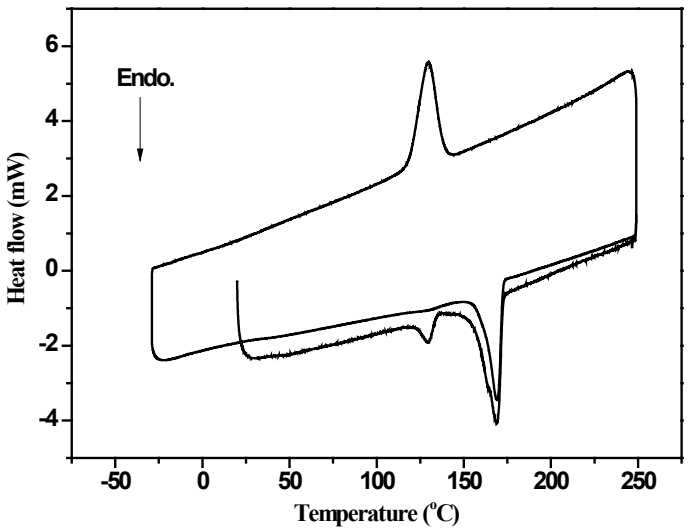

Figure S25. DSC traces of the as-prepared polyester PBF. Conditions: the sample was heated and cooled at a rate of 10 °C/min under nitrogen flow (25 mL/min).

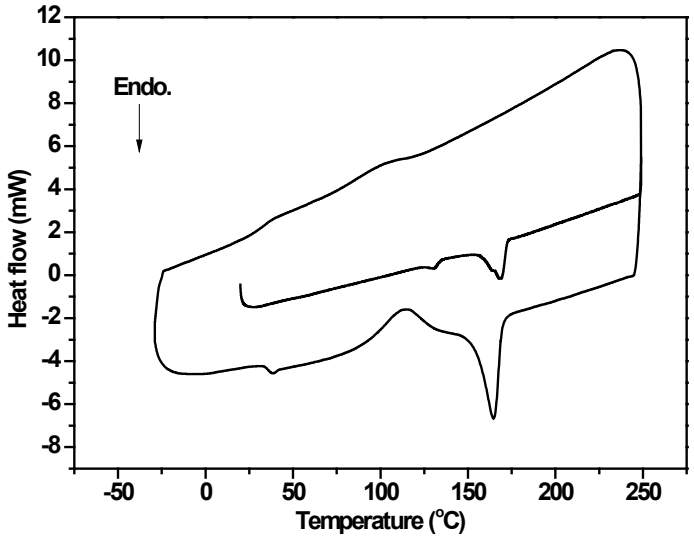

Figure S26. DSC traces of the as-prepared polyester PBF. Conditions: the sample was heated and cooled at a rate of 40 °C/min under nitrogen flow (25 mL/min).

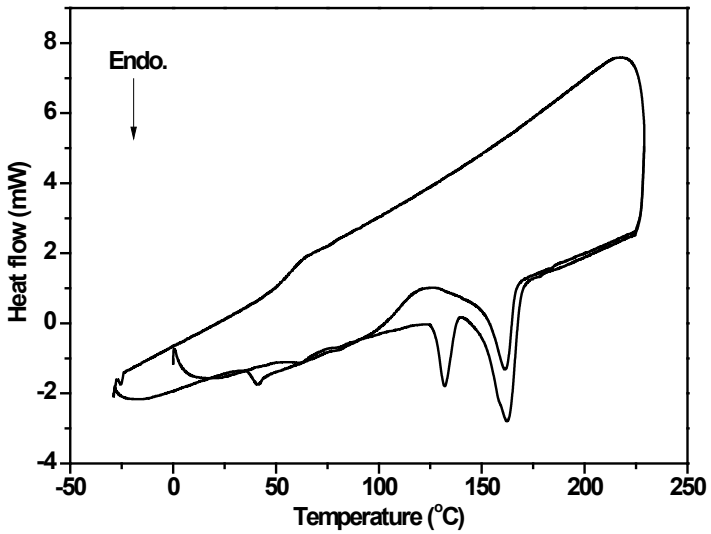

Figure S27. DSC traces of the as-prepared copolyester PEF/PBF-1/4. Conditions: the sample was heated and cooled at a rate of 40 °C/min under nitrogen flow (25 mL/min).

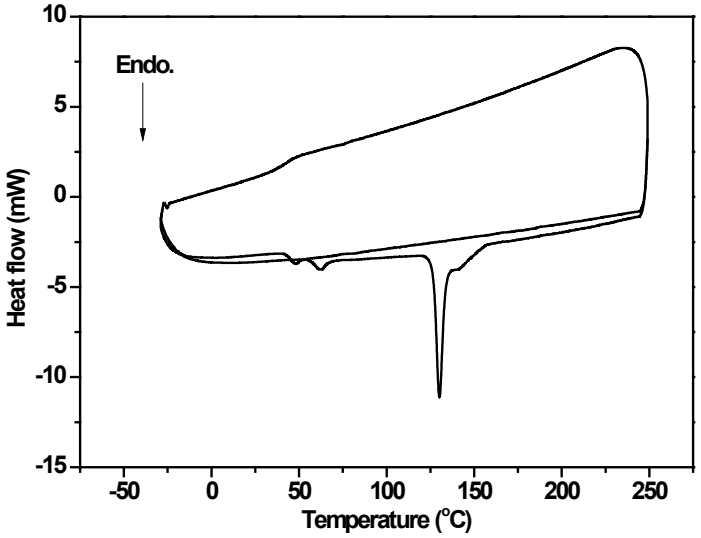

Figure S28. DSC traces of the as-prepared copolyester PEF/PBF-1/1. Conditions: the sample was heated and cooled at a rate of 40 °C/min under nitrogen flow (25 mL/min).

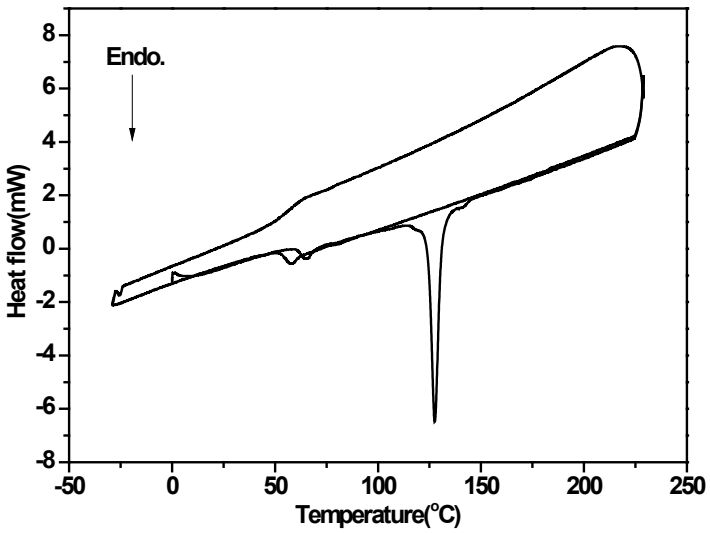

Figure S29. DSC traces of the as-prepared copolyester PEF/PBF-2/1. Conditions: the sample was heated and cooled at a rate of 40 °C/min under nitrogen flow (25 mL/min).

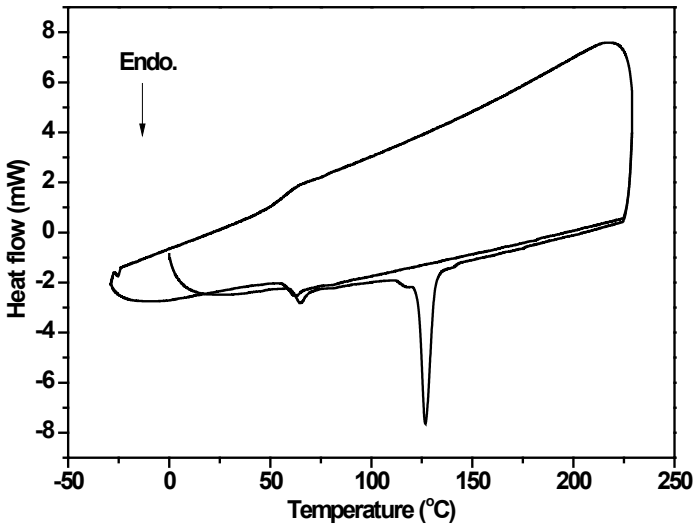

Figure S30. DSC traces of the as-prepared copolyester PEF/PBF-3/1. Conditions: the sample was heated and cooled at a rate of 40 °C/min under nitrogen flow (25 mL/min).

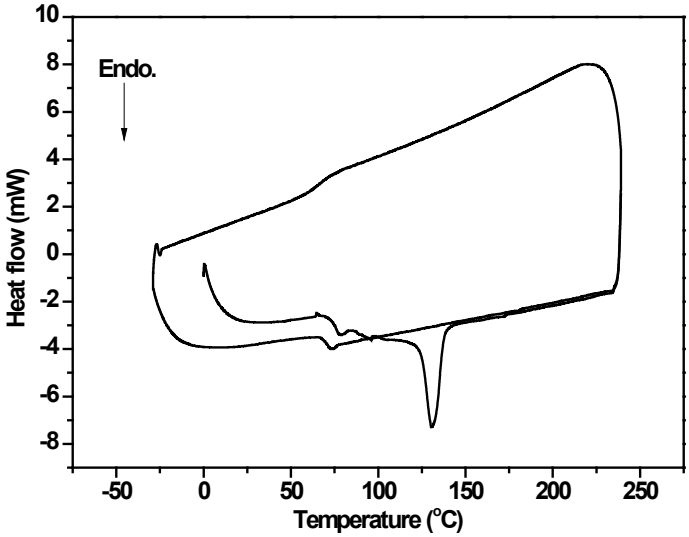

Figure S31. DSC traces of the as-prepared copolyester PEF/PBF-4/1. Conditions: the sample was heated and cooled at a rate of 40 °C/min under nitrogen flow (25 mL/min).

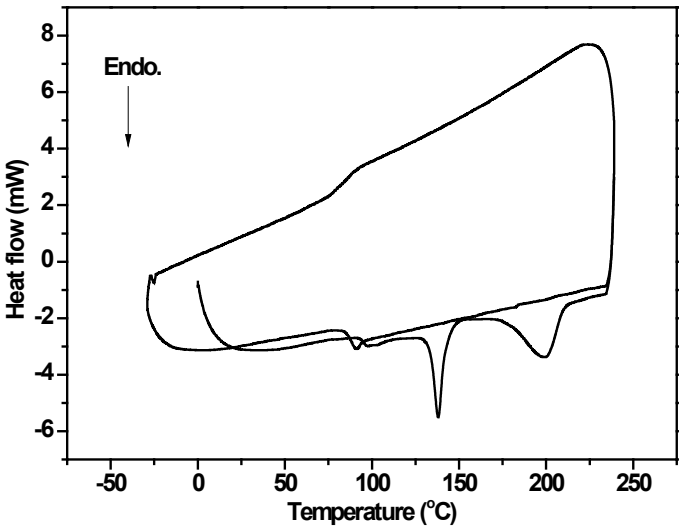

Figure S32. DSC traces of the as-prepared polyester PEF. Conditions: the sample was heated and cooled at a rate of 40 °C/min under nitrogen flow (25 mL/min).

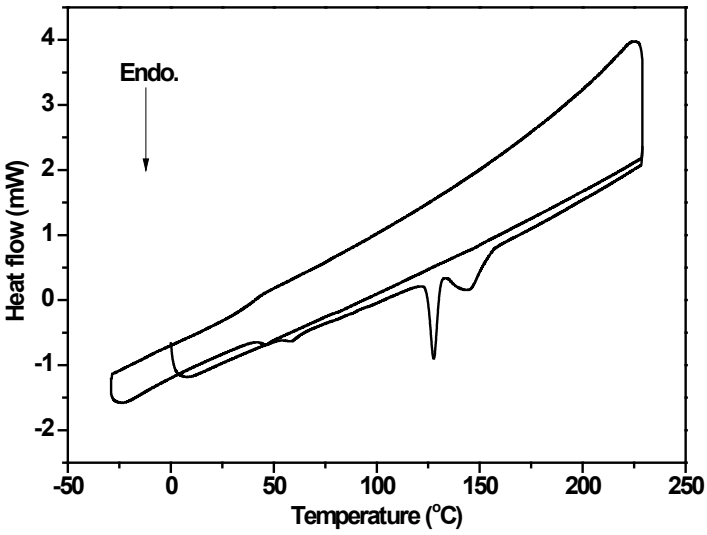

Figure S33. DSC traces of the as-prepared copolyester PEF/PBF-1/1. Conditions: the sample was heated and cooled at a rate of 10 °C/min under nitrogen flow (25 mL/min).