

Supplementary data

Thermally stable phthalonitrile resins based on multiple oligo (aryl ether)s with phenyl-s-triazine moieties in backbones

Lishuai Zong, Cheng Liu, Yujie Guo, Jinyan Wang*, and Xigao Jian

State Key Laboratory of Fine Chemicals, Department of Polymer Science and Materials, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China

*Corresponding Author: E-mail: wangjinyan@dlut.edu.cn

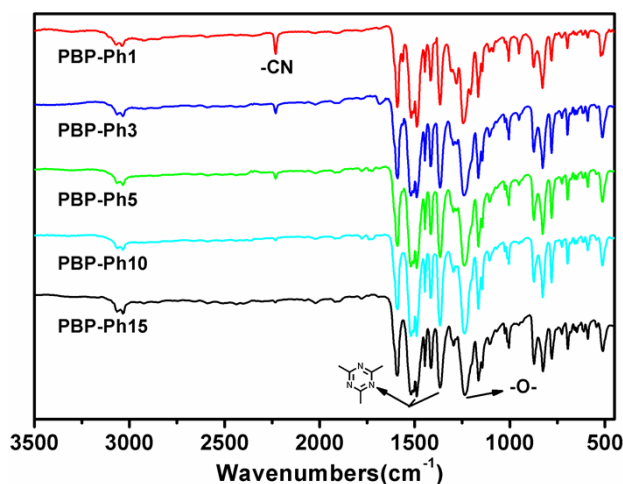


Fig. S1 FT-IR spectra of PBP-Phs.

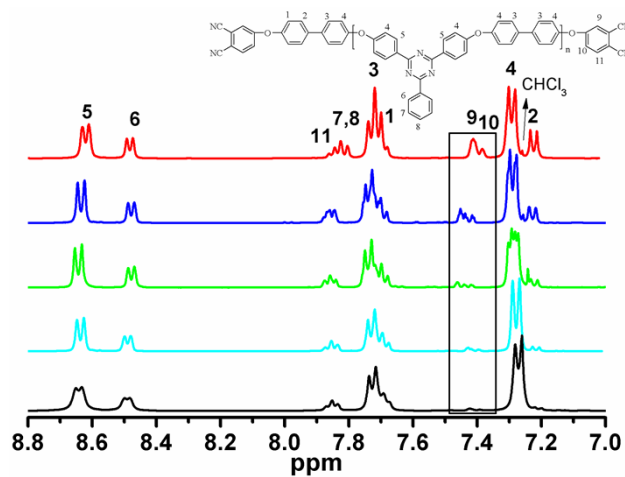


Fig. S2 ^1H -NMR spectra of PBP-Phs.

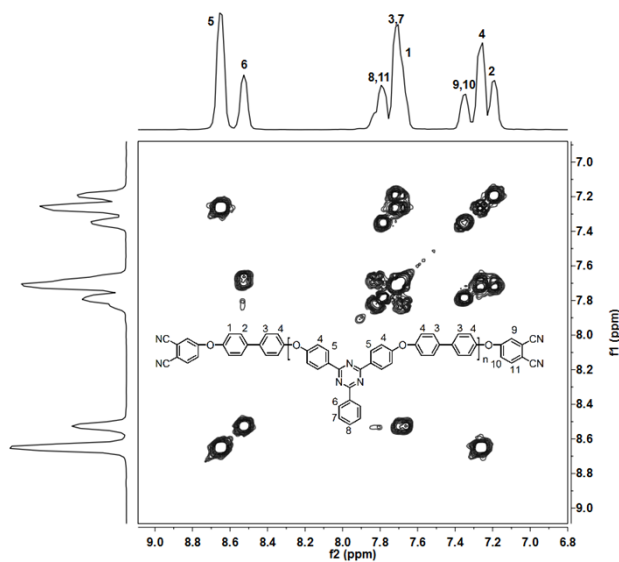


Fig. S3 ^1H - ^1H gCOSY spectrum ($\text{CDCl}_3+\text{CF}_3\text{COOD}$) of PBP-Ph1, with assignments.

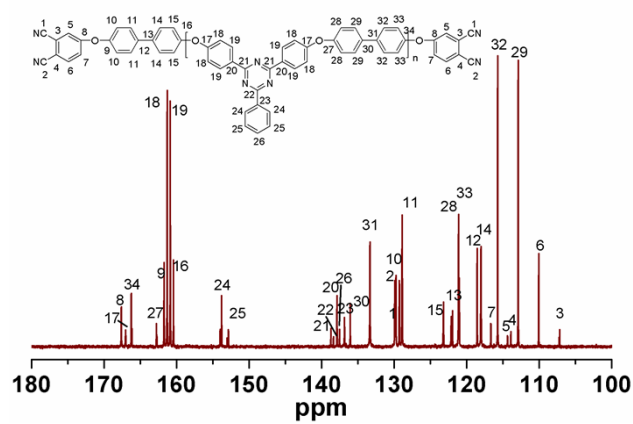


Fig. S4 ^{13}C -NMR spectrum ($\text{CDCl}_3+\text{CF}_3\text{COOD}$) of PBP-Ph5, with assignments.

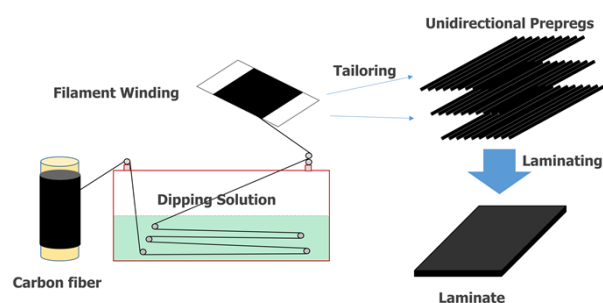


Fig. S5 The schematic diagram for the fabrication of the CF/Th-PBP composite laminates.

Fabrication process of the 7/T300 composites

All CF (T300) reinforced composites were fabricated *via* a similar procedure described as follows. 7.0 g oligomer was added to a three-necked flask and heated to melt at 250 °C (PBP-Ph1) or 280 °C (PBP-Ph3-10). 0.35 g BAPS was then added to the melted oligomer under vigorous stirring. The mixture was maintained at the melting temperature for 3-7 min, and then quenched to room temperature. The obtained B-stage resin was dissolved in 15 mL NMP. (The dipping solution of PBP-Ph15 was prepared by directly dissolving PBP-Ph15 and BAPS into NMP without undergoing B-stage resin formation.) The solution was equally poured onto sixteen plies of T300 CF weaves of 60×60×0.15 mm³. After dried at 60 °C on a horizontal heating board, all the prepregs were moved into a vacuum oven and maintained at 180 °C for 36 h and 200 °C for 1h. Then, the dried prepregs were compacted in a tight steel mold with a pressure of 2.5 MPa at 250 °C (PBP-Ph1) or 280 °C (PBP-Ph3-15) for 2 h. Then the steel mold was removed, and the laminate was cured at 250 °C for 1 h, 285 °C for 1 h, 325 °C for 3 h, 350 °C for 2 h, and 375 °C for 8 h in a muffle furnace. The thicknesses of all the finished laminates were approximately 2 mm. They should be sawed and sanded into 30×10×2 mm³ size for DMA test. The cross-sectional images of the laminates are shown in Fig. S6.

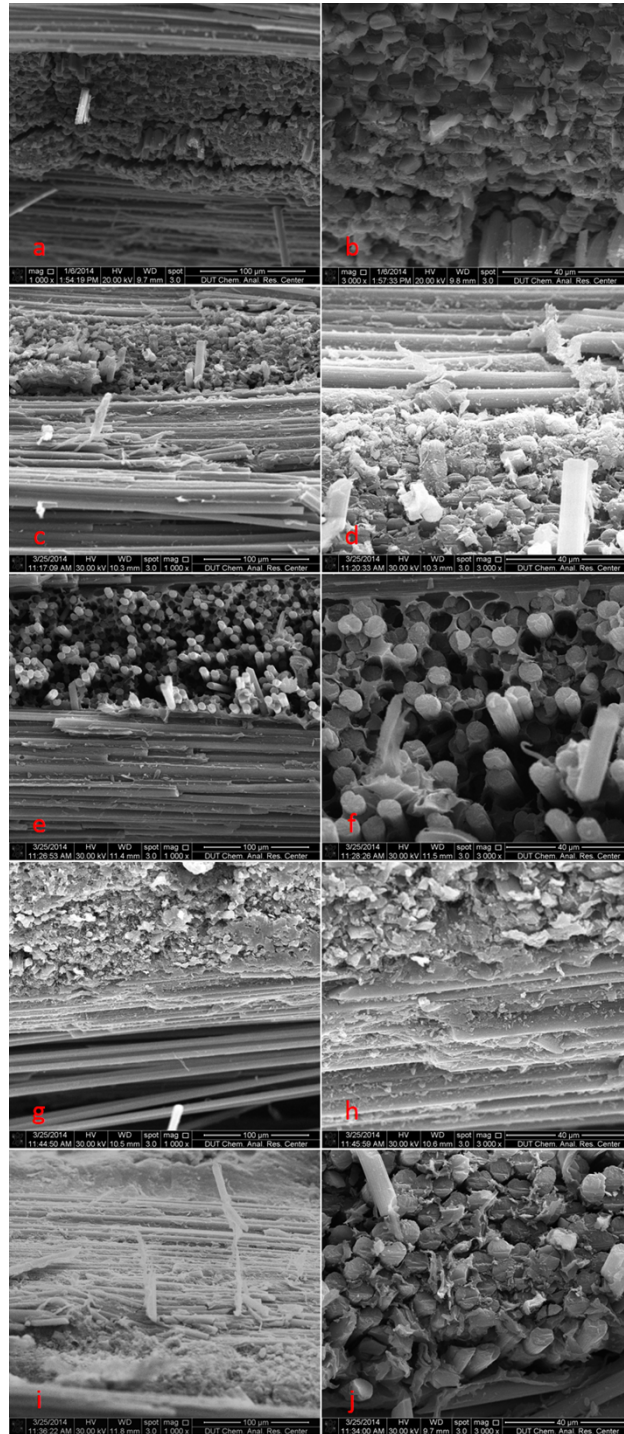


Fig. S6. The cross-sectional images for T300/Th-PBP laminates monitored by SEM instrument: (a, b) T300/Th-PBP1; (c, d) T300/Th-PBP3; (e, f) T300/Th-PBP5; (g, h) T300/Th-PBP10; (i, j) T300/Th-PBP15.

Table S1 Rheologic parameters of PBP-Phs

Sample	$T_m(^{\circ}\text{C})^a$	$ \eta^* _{\text{lowest}}(\text{Pa}\cdot\text{s})^b$	$T_{\eta<100}(^{\circ}\text{C})^b$	$t_{\text{gel}280}(\text{min})^c$	$ \eta^* _{\text{ini}280}(\text{Pa}\cdot\text{s})^c$
PBP-Ph1	211	2.7	218	9.3	7.0
PBP-Ph3	265	12.4	275	7.3	175.7
PBP-Ph5	265	34.7	316	5.9	195.8
PBP-Ph10	265	37.6	331	3.9	4414.0

a: detected by DSC; b: detected by rheometer without BAPS; c: detected by rheometer at 280°C with 5wt% BAPS.

Table S2 Thermal data of Th-PBPs.

Polymer	$T_g(^{\circ}\text{C})^a$	$T_{5\%}(^{\circ}\text{C})^b$	$T_{10\%}(^{\circ}\text{C})$	$T_{\text{max}}(^{\circ}\text{C})$	$C_{y800}^{\circ\text{C}}(\%)$	$C_{y900}^{\circ\text{C}}(\%)$	Gel Content (%) ^c
Th-PBP1	400	538(543) ^d	570(577)	589	71(16)	71(2)	97
Th-PBP3	349	559(574)	582(596)	596	68(21)	68(3)	97
Th-PBP5	302	562(575)	579(594)	594	61(11)	60(3)	96
Th-PBP10	298	571(575)	587(593)	593	62(0)	61(0)	95
Th-PBP15	294	582(575)	592(589)	601	61(0)	60(0)	95

^a The values was recorded on DMA at the heating rate of 3 °C/min.

^b The values was recorded on TGA at the heating rate of 20 °C/min in N₂ or air.

^c The gel contents were measured according to the ASTM D2765-11 standard.

^d The values in the brackets were recorded on TGA under air atmosphere.

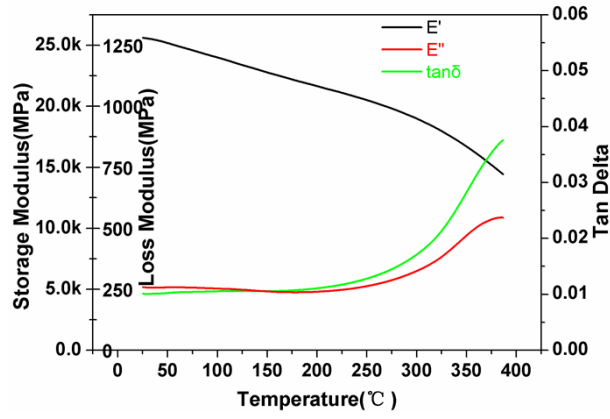


Fig. S7 DMA curves of T700/Th-PBP1 laminate.

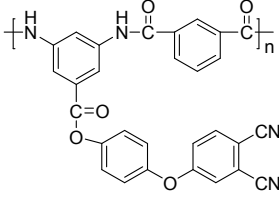
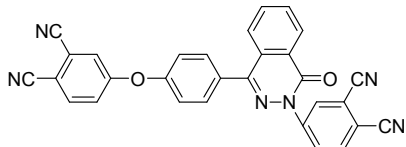
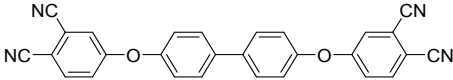
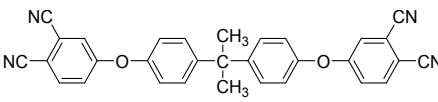
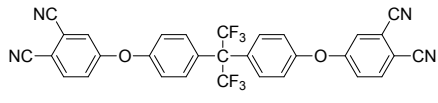
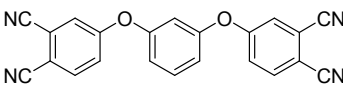
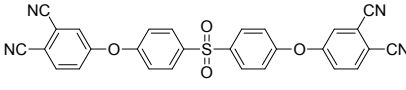
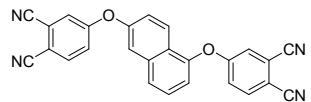
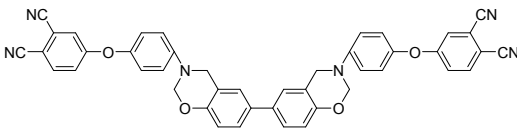
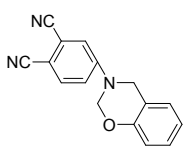
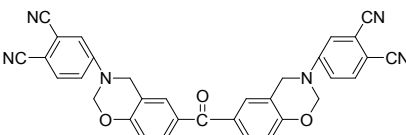
Table S3 Thermal property and processability comparison of PN resins.

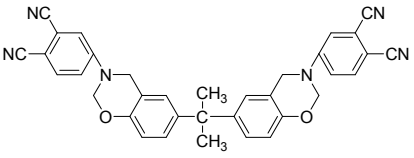
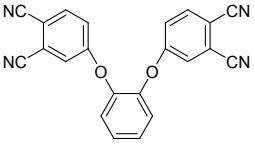
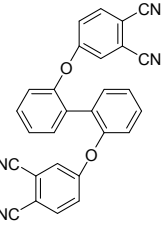
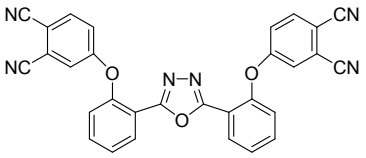
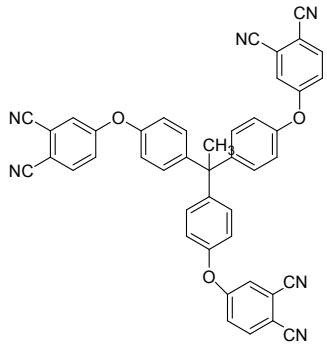
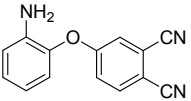
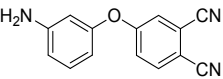
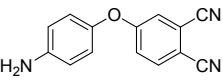
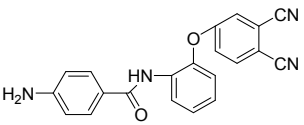
PN precursors	Chemical structure	T_g (°C)	$T_{d5\%,N_2}$ (°C)	$T_{d5\%,air}$ (°C)	Refs.
PN oligomer					
5		ca.400	538	543	-
5		ca.400	555	552	-
xo-HEI(1)	Ar:	-	540	-	1
xo-REI(5)		-	521	-	1
xo-BEI(1)		-	550	-	1
6	R:	370	ca.500 ^f	ca.525	2
6A		>310	ca.500 ^f	-	3
6A'		>310	ca.500 ^f	-	3
N=2		240	506	501	4
1		ca. 450	495	505	5
1a		>400	490	490	6
1b		>400	490	495	6

PEN-t-Ph		188	525	-	7
2CN-o-PEEK		208	517	-	8
2PEN-BPh		>450	560	518	9
2PEN-BAPh		-	512	512	10
PAEK-CN		>400	515	516	11
5		>300	ca.540'	ca500	12

Polymer with pendent PN units

PEN-CN3		213	475	-	13
					14
PI-4a	Ar:	220	509	-	14
PI-4b		234	529	-	14
PI-4c		209	520	-	14

CN-PA		325	380	-	15
	PN monomer				
HHPZ-PH		- ^a	514	528	16
BPh		>450	511	517	17
BAPh		>450	ca.515 ^f	ca.545 ^f	17
6FPH		>450	485	485	17
RPh		>400	ca.505 ^f	ca.510 ^f	18
BDS		337	436	441	19
1,6-BDCN		>465	553	549	20
BZBPH		-	478	482	21
I		316	450	420	22
III		-	544	390	22

IV		330	423	-	22
1		350	444	437	23
2		>450	490	488	23
3		>500	512	500	23
TDPE		>380	556	543	24
Self-promoted PN monomer					
2O		582	527	505	25
2M		565	524	512	25
2P		580	528	518	25
3a		>500	517	496	26

3b		>500	506	501	26
3c		>500	531	502	26
4O		450	529	520	27
4M		420	525	514	27
4P		450	528	514	27
HSiPN		>450	535	558	28
MeSiPN		424	541	543	28
ViSiPN		428	570	562	28
DBPA-Ph		>350	478	464	29
BIPN		>325	540	535	30
PIPn		-	516	518	31
3PN3PEOD PA		>400	516	-	32

^a The specific data was not mentioned or different to read from the relevant figures.

^fThe values were roughly read from the relevant figures in order to make comparisons.

References

1. C. Liu, J. Y. Wang, E. C. Lin, L. S. Zong and X. G. Jian, *Polym. Degrad. Stab.* , 2012, **97**, 460-468.
2. M. Laskoski, D. D. Dominguez and T. M. Keller, *J. Polym. Sci., Part A: Polym. Chem.* , 2005, **43**, 4136-4143.
3. T. M. Keller, *Chem. Mater.* , 1994, **6**, 302-305.
4. D. D. Dominguez and T. M. Keller, *High Perform. Polym.* , 2006, **18**, 283-304.
5. M. Laskoski, D. D. Dominguez and T. M. Keller, *J. Polym. Sci., Part A: Polym. Chem.* , 2013, **51**, 4774-4778.
6. M. Laskoski, D. D. Dominguez and T. M. Keller, *Polymer*, 2007, **48**, 6234-6240.
7. Y. Zou, J. Yang, Y. Zhan, X. Yang, J. Zhong, R. Zhao and X. Liu, *J. Appl. Polym. Sci.* , 2012, **125**, 3829-3835.
8. H. Zhang, T. Liu, W. Yan, Y. Su, H. Yu, Y. Yang and Z. Jiang, *High Perform. Polym.* , 2014, **26**, 1007-1014.
9. X. Yang, J. Zhang, Y. Lei, J. Zhong and X. Liu, *J. Appl. Polym. Sci.* , 2011, **121**, 2331-2337.
10. R. Du, W. Li and X. Liu, *Polym. Degrad. Stab.* , 2009, **94**, 2178-2183.
11. T. Liu, Y. Yang, T. Wang, H. Wang, H. Zhang, Y. Su and Z. Jiang, *Polym. Eng. Sci.* , 2014, **54**, 1695-1703.
12. T. M. Keller, *Polymer*, 1993, **34**, 952-955.
13. J. Yang, X. L. Yang, Y. K. Zou, Y. Q. Zhan, R. Zhao and X. B. Liu, *J. Appl. Polym. Sci.* , 2012, **126**, 1129-1135.
14. K. Zeng, Y. Zou and G. Yang, *Des. Monomers Polym.* , 2014, **17**, 186-193.
15. K. Zeng, H. B. Hong, S. H. Zhou, D. M. Wu, P. K. Miao, Z. F. Huang and G. Yang, *Polymer*, 2009, **50**, 5002-5006.
16. G. P. Yu, C. Liu, X. P. Li, J. Y. Wang, X. G. Jian and C. Y. Pan, *Polym. Chem.* , 2012, **3**, 1024-1032.
17. S. B. Sastri and T. M. Keller, *J. Polym. Sci., Part A: Polym. Chem.* , 1999, **37**, 2105-2111.
18. T. M. Keller and D. D. Dominguez, *Polymer*, 2005, **46**, 4614-4618.
19. X. Peng, H. Sheng, H. Guo, K. Naito, X. Yu, H. Ding, X. Qu and Q. Zhang, *High Perform. Polym.* , 2014, **26**, 837-845.
20. F. Zhao, R. Liu, C. Kang, X. Yu, K. Naito, X. Qu and Q. Zhang, *RSC Adv.* , 2014, **4**, 8383-8390.
21. F. Zuo and X. Liu, *J. Appl. Polym. Sci.* , 2010, **117**, 1469-1475.
22. Z. Brunovska, R. Lyon and H. Ishida, *Thermochim. Acta* 2000, **357-358**, 195-203.
23. A. Badshah, M. R. Kessler, H. Zhou and A. Hasan, *Polym. Int.* , 2014, **63**, 465-469.
24. H. Sheng, X. Peng, H. Guo, X. Yu, C. Tang, X. Qu and Q. Zhang, *Mater. Chem. Phys.* , 2013, **142**, 740-747.
25. H. Zhou, A. Badshah, Z. Luo, F. Liu and T. Zhao, *Polym. Adv. Technol.* , 2011, **22**, 1459-1465.
26. A. Badshah, M. R. Kessler, H. Zhou, J. H. Zaidi, S. Hameed and A. Hasan, *Polym. Chem.* , 2013, **4**, 3617-3622.
27. B. Amir, H. Zhou, F. Liu and H. Aurangzeb, *J. Polym. Sci., Part A: Polym. Chem.* , 2010, **48**, 5916-5920.
28. Z. B. Zhang, Z. Li, H. Zhou, X. K. Lin, T. Zhao, M. Y. Zhang and C. H. Xu, *J. Appl. Polym. Sci.* , 2014, **131**.

29. X. Q. Zou, M. Z. Xu, K. Jia and X. B. Liu, *J. Appl. Polym. Sci.* , 2014, **131**, 41203-41209.
30. D. M. Wu, Y. C. Zhao, K. Zeng and G. Yang, *J. Polym. Sci., Part A: Polym. Chem.* , 2012, **50**, 4977-4982.
31. J. Hu, Y. Liu, Y. Jiao, S. Ji, R. Sun, P. Yuan, K. Zeng, X. Pu and G. Yang, *RSC Adv.* , 2015, **5**, 16199-16206.
32. P. Yuan, Y. Liu, K. Zeng and G. Yang, *Des. Monomers Polym.* , 2015, **18**, 343-349.