Supporting information

Micro-Branched Crosslinked Photosensitive Polyimides (PSPIs): Optimizing Dielectric, Thermal, and Lithographic Performance

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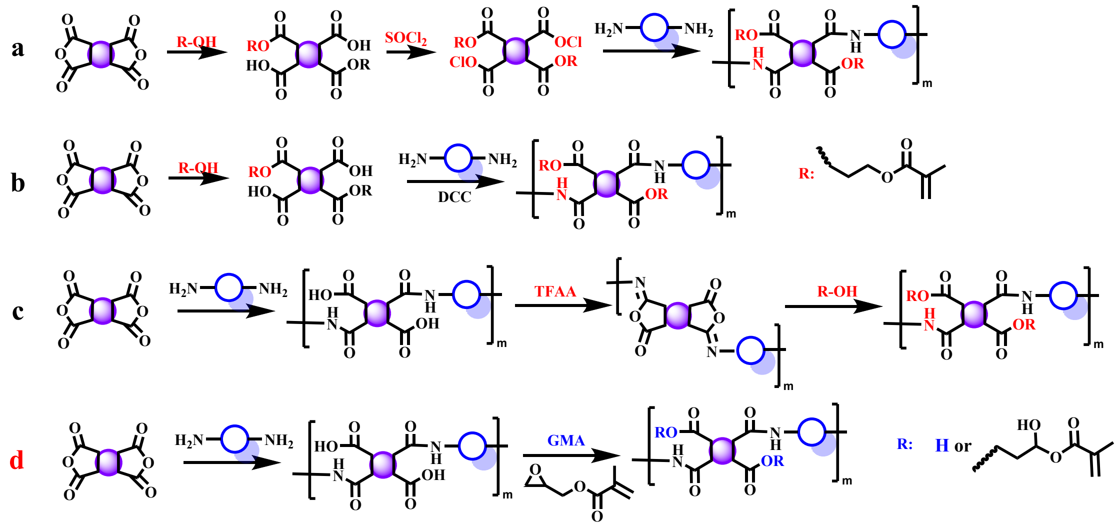

Figure S1. Three classical methods for the synthesis of photosensitive polyamide esters: (a) acyl chloride method (b) DCC method (c) polyisoimide method and (d) GMA method.

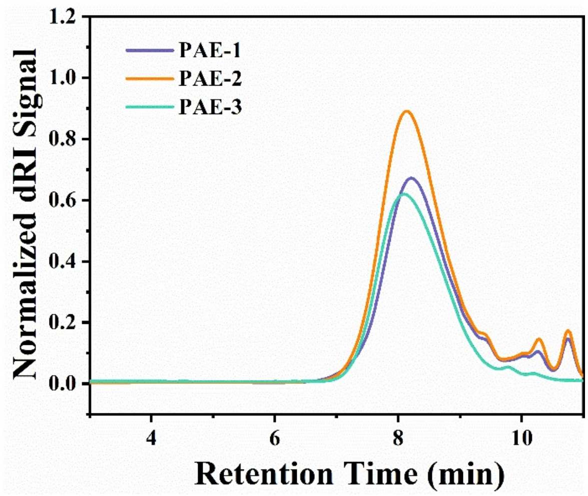

Figure S2. GPC curves showing the molecular weight distributions of **PAE-1**, **PAE-2**, and **PAE-3.**

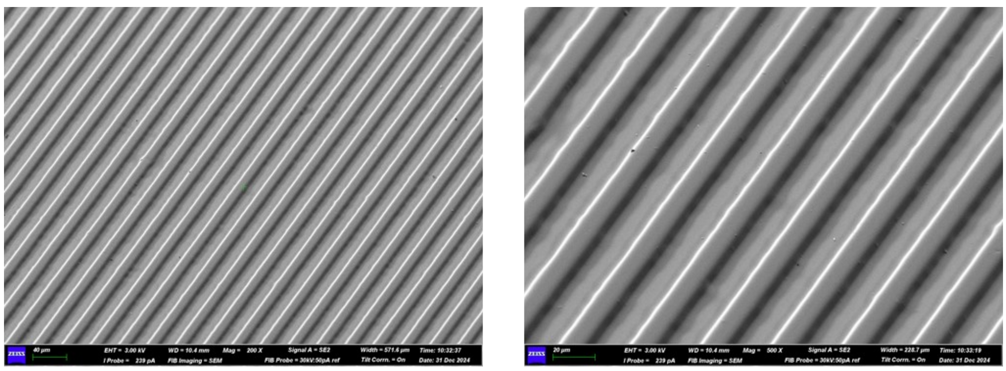

Figure S3. PAE-2 with 10 wt% photoinitiators exposure development results.

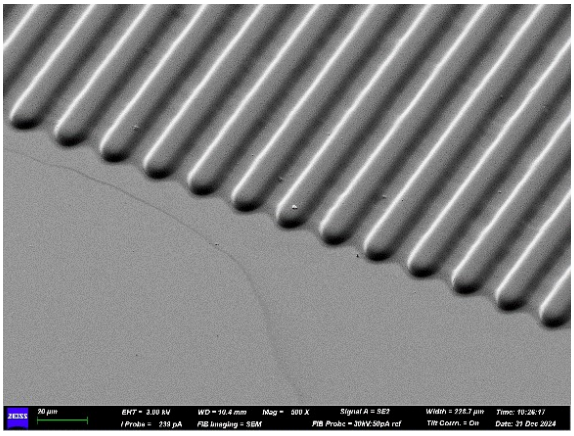

Figure S4. PAE-1 resin contains 5 wt% photoinitiators exposure development results.

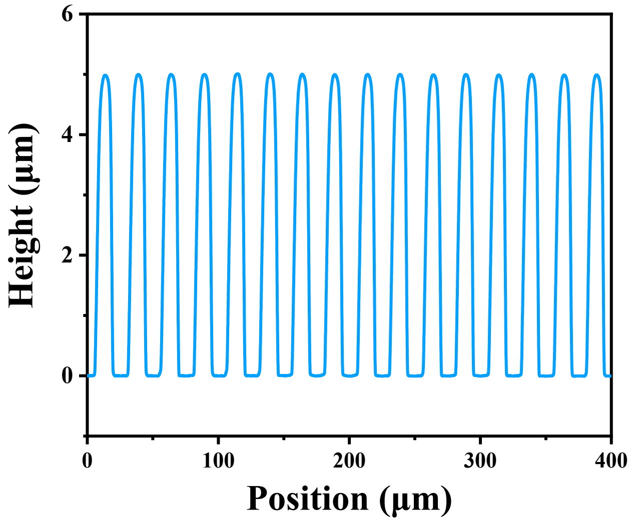

Figure S5. PSPI-2 Film thickness curve after high temperature curing.

Table S1. The D_k, D_f and the maximum patterning resolution of the reported photosensitive polyimides.

Sample name	Maximum resolution (μm)	D_k	D_f	Ref.
PSPI-2	**5**	**2.77 (10Ghz)**	**0.0135 (10Ghz)**	**This work**
PSPI-2	10	3.16 (5Ghz)	0.0098 (5Ghz)	1
n-PSPI-2	7	2.73 (10Ghz)	0.0032 (10Ghz)	2
n-LTPI-IMZ-2.0	5	2.8 (10Ghz)	0.0058 (10Ghz)	3
PI-PyF$_{5\%}$-200	3	3.18 (10Ghz)	0.00241 (10Ghz)	4
C-PI-3	5	2.93 (10Ghz)	0.0096 (10Ghz)	5

Table S2. Synthesis parameters of PAE via polycondensation and graft modification

Name	samples	6FDA (mmol)	TFMB (mmol)	POB (mmol)	PB (mmol)
PAE-1	6FDA-TFMB	15	15	-	-
---	6FDA-TFMB-1%POB[a]	15	14.85	0.1	-
PAE-2	6FDA-TFMB-2%POB[a]	15	14.7	0.2	-
---	6FDA-TFMB-3%POB[a]	15	14.55	0.3	-
---	6FDA-TFMB-1%PB[b]	15	14.85	-	0.1
---	6FDA-TFMB-2%PB[b]	15	14.7	-	0.2
PAE-3	6FDA-TFMB-3%PB[b]	15	14.55	-	0.3

[a] POB (x mol%) content relative to the total -NH_2 groups derived from TFMB and POB.

[b] PB (x mol%) content relative to the total -NH_2 groups derived from TFMB and PB.

Table S3. The esterification degree and molecular weight of PAE 1-3 resin

Sample	M_n (g/mol)	M_w (g/mol)	*Đ*
PAE-1	9600	19900	2.07
PAE-2	9800	19200	1.95
PAE-3	10500	21500	2.04

Table S4. Grafting rate of PAE-1 with different reaction time

Time (h)	Ar-H Integral area	C=CH_2 Integral area	DOE (%)
1	12	0.18	4.5
2	12	0.85	21.3
3	12	1.29	32.3
4	12	1.34	33.7
5	12	1.35	33.8
6	12	1.42	35.4

Ar-H 7.0~8.5 =CH_2 (5.5~6.1).

Table S5. Grafting rate of PAE-2 with different reaction time

Time (h)	Ar-H Integral area	$C=CH_2$ Integral area	DOE (%)
1	12.1	0.96	24.0
2	12.1	1.48	37.0
3	12.1	1.67	41.8
4	12.1	1.65	41.3
5	12.1	1.62	40.5
6	12.1	1.68	42.0

Ar-H 7.0~8.5 $=CH_2$ (5.5~6.1)

Table S6. Grafting rate of PAE-3 with different reaction time

Time (h)	Ar-H Integral area	$C=CH_2$ Integral area	DOE (%)
1	12.1	0.68	17
2	12.1	1.34	33.5
3	12.1	1.98	49.5
4	12.1	2.00	50.0
5	12.1	2.08	52.0
6	12.1	2.12	53.0

Ar-H 7.0~8.5 $=CH_2$ (5.5~6.1)

Table S7. Mechanical and thermal properties of the resulting PSPI 1-3 films

	Thermal properties				Mechanical properties				
	TGA			DSC	TMA				
Samples	$T_{d,5\%}$ [°C]	$T_{d,30\%}$ [°C]	$^{a}T_{HRI,}$ [°C]	T_g [°C]	T_g [°C]	CTE ppm/K	σ_{max} [MPa]	ε_b [%]	E [GPa]
I	384	581	246.1	--	283.3	86.1	105.2	1.8	6.6
II	436	586	287.1	--	297.7	54.3	123.3	2.2	7.9
III	483	595	291.6	--	305.5	59.4	134.7	2.3	8.7

a:$T_{HRI} = 0.49 \times [T_{d,5\%} + 0.6 * (T_{d,30\%} - T_{d,5\%})]$;

Reference：

1. Lai, X.; Zhang, J.; Yang, Z.; Huang, S.; Li, J.; Zhang, G.; Sun, R. Synthesis of Poly(amic Ester) with Controlled Molecular Weight for Photosensitive Polyimide in Advanced Package. *Mater. Today Commun.* 2023, **37**, 107316–107325.
2. Ma, J.-X.; Yuan, L.-L.; Fan, S.-N.; Wang, L.-Z.; Jia, B.; Yang, H.-X.; Yang, S.-Y. Negative-Tone Photosensitive Polyimide with High Transparency. *Eur. Polym. J.* 2023, **192**, 112071–112078.
3. Fan, S. N.; Yuan, L. L.; Wang, L. Z.; Jia, B.; Ma, J. X.; Yang, H. X.; Yang, S. Y. Low-Temperature Curable Negative-Tone Photosensitive Polyimides: Structure and Properties. Polymers 2023, **15**, 973–985.
4. Huang, S.; Lv, X.; Lai, X.; Li, J.; Zhang, Y.; Qiu, S.; Zhang, G.; Sun, R. A Strategy to Prepare Low-Temperature Curable Photosensitive Polyimide with Good Comprehensive Performance. Chem. Eng. J. 2023, **477**, 146858–146869.
5. Meng, H.; Chen, K.; Li, C.; Zhang, L.; He, Y.; Zhao, Z.; Wu, P.; Zhu, H.; Chi, Z.; Xu, J.; Liu, S.; Zhang, Y. Innocuous Solvent-Based, Low-Temperature Curable, and Highly Transparent Photosensitive Polyimides Developed Using Soluble Polyimides Containing Bio-Based Magnolol Moieties. Chem. Sci. 2025, **16**, 3157–3167.