Electronic Supplementary Information for

Temperature for curing phthalonitrile-terminated poly(phthalazinone ether

nitrile) reduced by a mixed curing agent and its curing behavior

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Fig. S1. ¹H NMR spectra (400 M, CDCl₃, 25 °C) of PPEN-Ph

- **Fig. S2.** DSC curves of the curing reaction with BAS at different heating rates (1: 5 °C/min; 2: 10 °C/min; 3: 15 °C/min; and 4: 20 °C/min)
- **Fig. S3.** DSC curves of the curing reaction with ZnCl₂ at different heating rates (1: 5 °C/min; 2: 10 °C/min; 3: 15 °C/min; and 4: 20 °C/min)
- **Fig. S4.** DSC curves of the curing reaction with AMTU at different heating rates (1: 5 °C/min; 2: 10 °C/min; 3: 15 °C/min; and 4: 20 °C/min)

Fig. S5. Heating rate versus curing temperature of maximum peak line graph of BAS

- Fig. S6. Heating rate versus curing temperature of maximum peak line graph of ZnCl₂
- Fig. S7. Heating rate versus curing temperature of maximum peak line graph of AMTU

Table S1. The DSC curves with BAS at different heating rates

Table S2. The DSC curves with ZnCl₂ at different heating rates

Table S3. The data of DSC curves with AMTU at different heating rates

Calculate Ea via Kissinger and Ozawa equation



Fig. S1. ¹H NMR spectra (400 M, CDCl₃, 25 °C) of PPEN-Ph.



Fig. S2. DSC curves of the curing reaction with BAS at different heating rates. a): 5 °C·min⁻¹; b): 10 °C·min⁻¹; c): 15 °C·min⁻¹; d): 20 °C·min⁻¹.



Fig. S3. DSC curves of the curing reaction with ZnCl₂ at different heating rates. a): 5 °C·min⁻¹;
b): 10 °C·min⁻¹; c): 15 °C·min⁻¹; d): 20 °C·min⁻¹.



Fig. S4. DSC curves of the curing reaction with AMTU at different heating rates. a): 5 °C·min⁻¹; b): 10 °C·min⁻¹; c): 15 °C·min⁻¹; d): 20 °C·min⁻¹.



Fig. S5. Heating rate versus curing temperature of maximum peak over BAS.



Fig. S6. Heating rate versus curing temperature of maximum peak over ZnCl₂.



Fig. S7. Heating rate versus curing temperature of maximum peak over AMTU.

Heating rate / $^{\circ}C \cdot min^{-1}$	$T_{\rm p}$ / °C	$T'_{p} / °C$
5	259	342
10	280	353
15	291	364
20	307	373

 Table S1
 The DSC curves with BAS at different heating rates

Table S2 The DSC curves with $ZnCl_2$ at different heating rates

Heating rate / °C·min ⁻¹	$T_{\rm p}$ / °C	<i>T′</i> _p / °C
5	274	371
10	278	376
15	279	382
20	289	397

Table S3 The data of DSC curves with AMTU at different heating rates

Heating rate / °C·min ⁻¹	<i>T</i> _p / °C	<i>T</i> ′ _p / °C
5	235	345
10	246	349
15	261	360
20	270	362

Calculate Ea via Kissinger and Ozawa equation

The apparent activation energy Ea of the curing reaction is an important parameter to measure the curing reactivity of a curing system. It reflects the difficulty level of the curing reaction. The larger the Ea is, the higher curing temperature is generally required. This makes the reaction rate more sensitive to temperature. Thus, the apparent activation energy has a very vital significance to the research of curing reaction.¹ The apparent activation energy of the curing reaction in resin systems could be calculated via the Kissinger equation^{2,3} and the Ozawa equation.⁴

Kissinger equation:

$$\frac{\mathrm{d}\left[\ln\left(\beta/T_{\mathrm{p}}^{2}\right)\right]}{\mathrm{d}\left(1/T_{\mathrm{p}}\right)} = -\frac{Ea}{R}$$

where β is the heating rate, °C·min⁻¹; T_p is the temperature of maximum peak, K; *Ea* is the apparent activation energy, kJ/mol; and *R* is the Gas constant, 8.314 J·K⁻¹·mol⁻¹.

Ozawa equation:

$$\frac{\mathrm{d}\left[\ln\beta\right]}{\mathrm{d}\left(1/T_{\mathrm{p}}\right)} = -\frac{1.052Ea}{R}$$

where β is the heating rate, °C·min⁻¹; T_p is the temperature of maximum peak, K; *Ea* is the apparent activation energy, kJ·mol⁻¹; and *R* is the Gas constant, 8.314 J·K⁻¹·mol⁻¹.

References

- 1 Y. Fan, K. Sun and R. Wu, Polym. Mater. Sci. & Eng., 2001, 17, 60.
- 2 H. E. Kissinger, Anal. Chem., 1957, 29, 1702.
- 3 A. Catalani and M. G. Bonicelli, *Thermochim. Acta*, 2005, 438, 126.

4 T. Ozawa, Bull. Chem. Soc. Jpn, 1965, **38**, 1881.