Supporting Information

Smart and Sustainable Design of Latent Catalyst-Containing Benzoxazine-Bio-Resins and Application Studies

Kan Zhang,*[a] Yuqi Liu,[a] Mengchao Han,[a] and Pablo Froimowicz*[b]

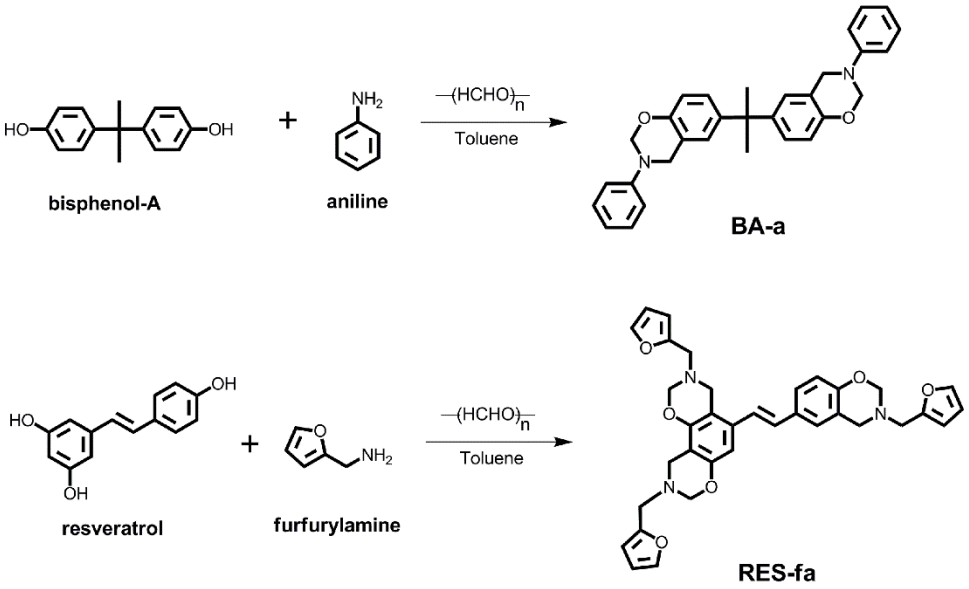
[a] Research School of Polymeric Materials, School of Materials Science and Engineering, Jiangsu University, Zhenjiang, Jiangsu 212013, P. R. China

[b] Design and Chemistry of Macromolecules Group, Institute of Technology in Polymers and Nanotechnology (ITPN), UBA-CONICET, FADU, University of Buenos Aires, Pabellón III, subsuelo, Ciudad Universitaria (C1428EGA), Buenos Aires, Argentina

*: To whom correspondence should be addressed:

Kan Zhang: zhangkan@ujs.edu.cn

Pablo Froimowicz: pxf106@case.edu



Scheme S1. Synthesis of BA-a and RES-fa.

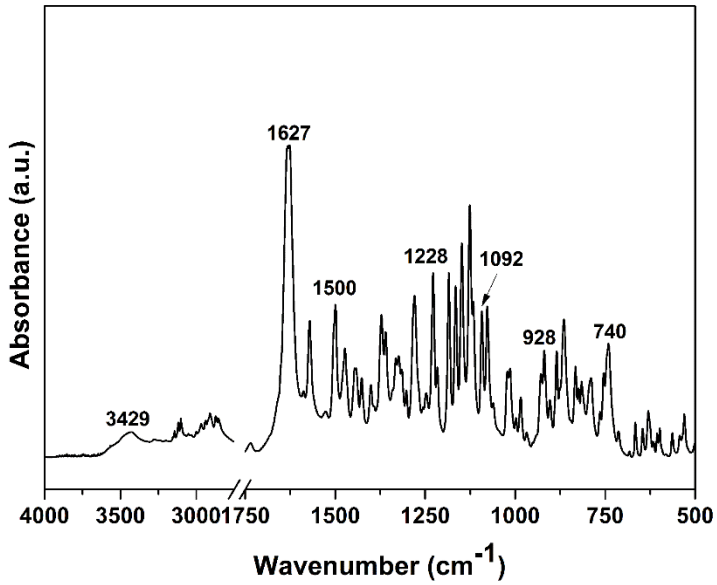


Figure S1. FT-IR spectrum of **NAR-fa**.

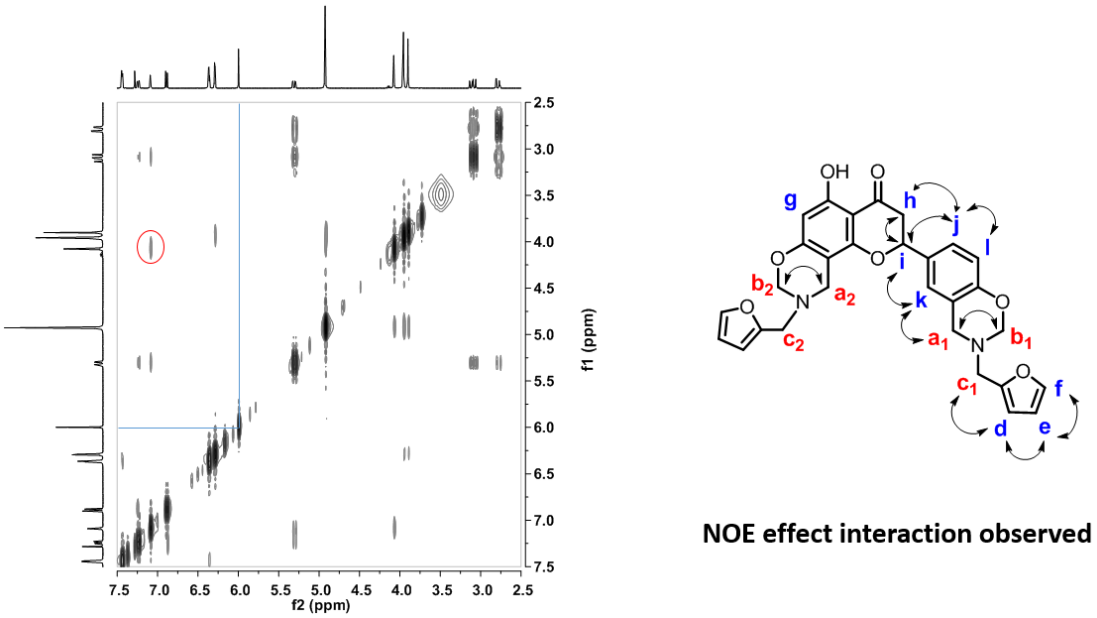


Figure S2. 2D ^{1}H-^{1}H NOESY NMR spectrum of **NAR-fa**.

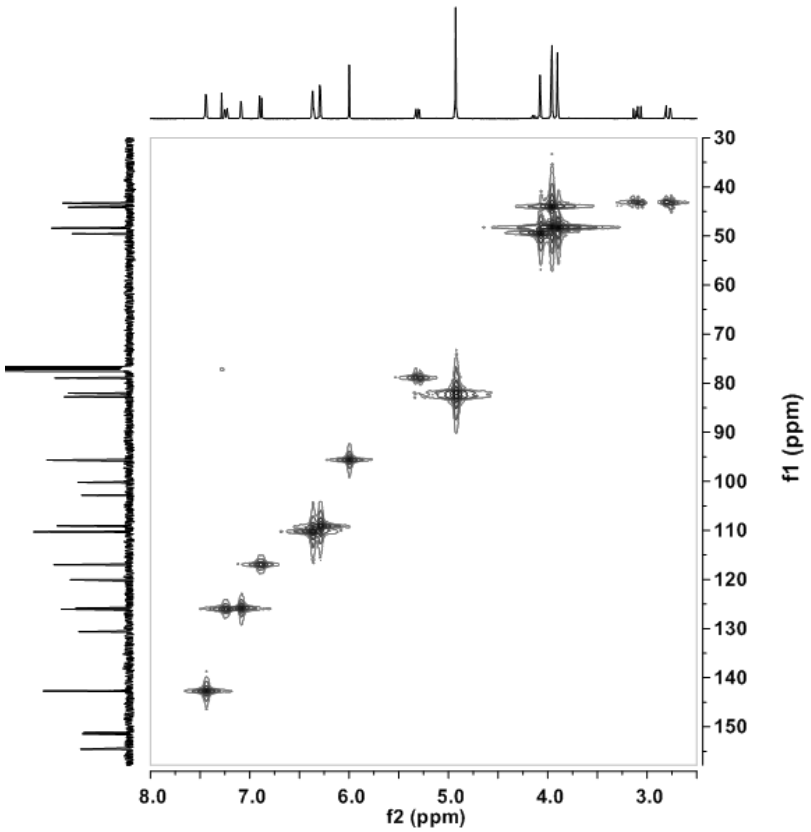


Figure S3. 2D ^{1}H-^{13}C HMQC NMR spectrum of **NAR-fa**.

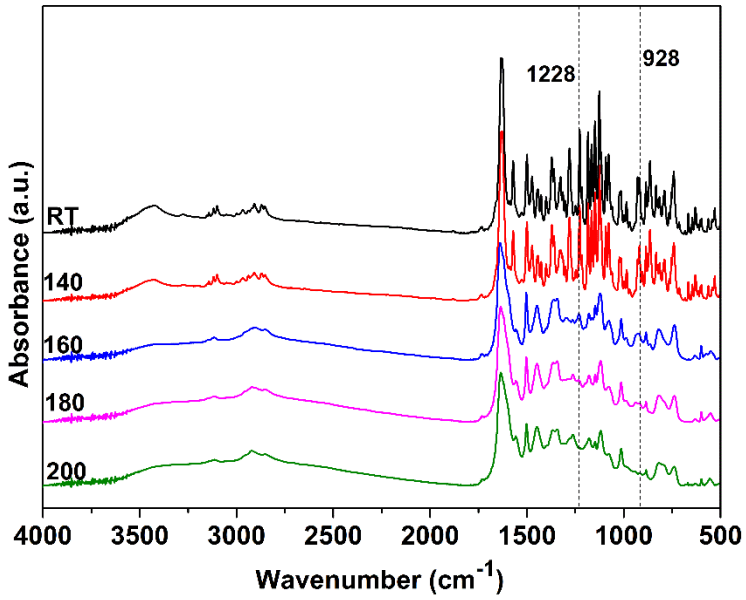


Figure S4. *In situ* FT-IR spectra of **NAR-fa** during the step by step polymerization reaction.

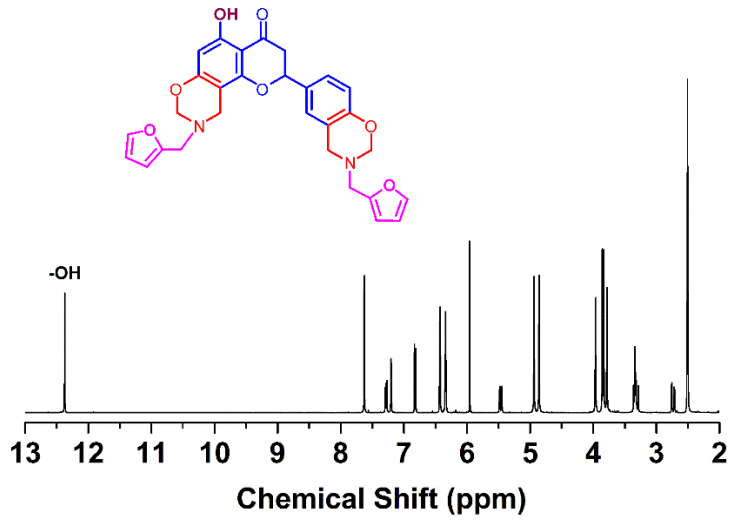


Figure S5. ^{1}H NMR spectrum of **NAR-fa** in DMSO-d_6.

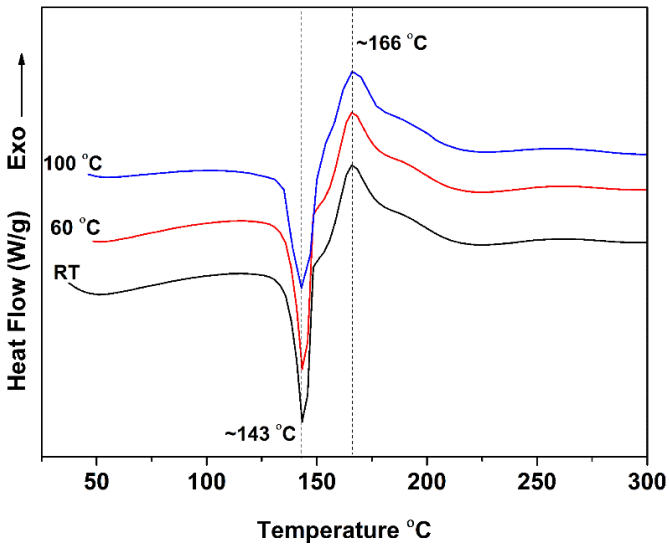


Figure S6. DSC thermograms of **NAR-fa** (in black, bottom), the one pretreated at 60 °C for 1h (in red, middle), and that pretreated at 100 °C for 1h (in blue, top).

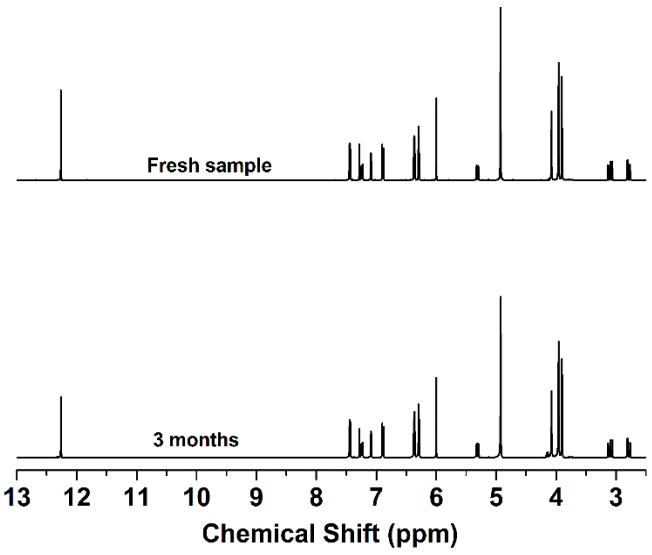


Figure S7. 1H NMR spectra of **NAR-fa** in $CDCl_3$ and that stored in the dark for 3 months.

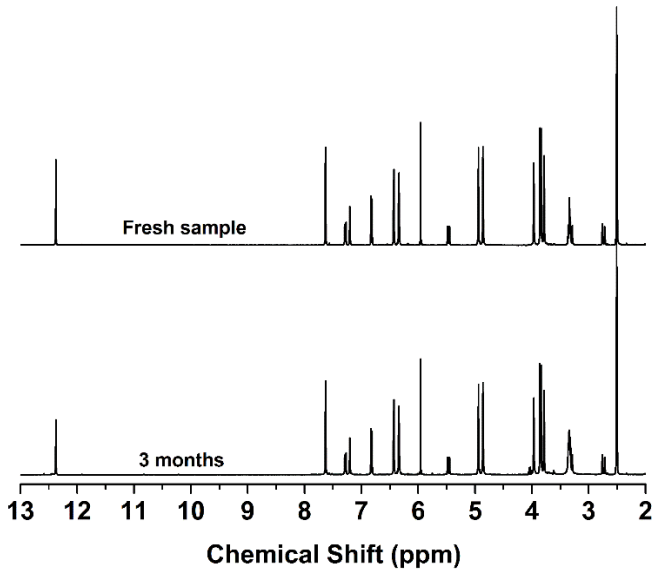


Figure S8. ^{1}H NMR spectra of **NAR-fa** in DMSO-d_6 and that stored in the dark for 3 months.

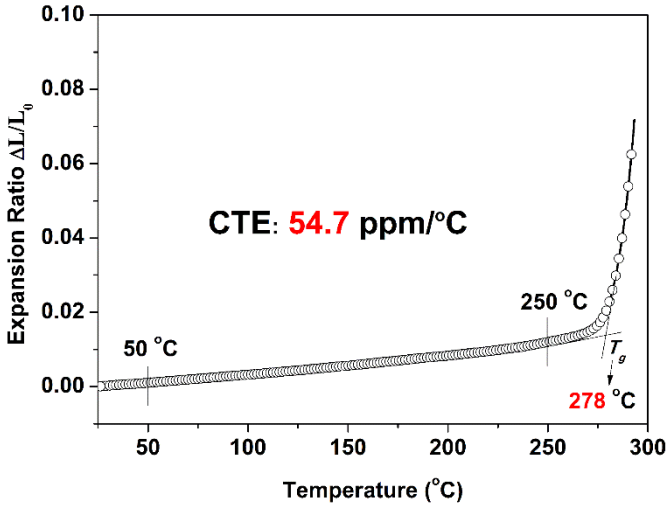


Figure S9. Thermomechanical analysis of **poly(NAR-fa)**.

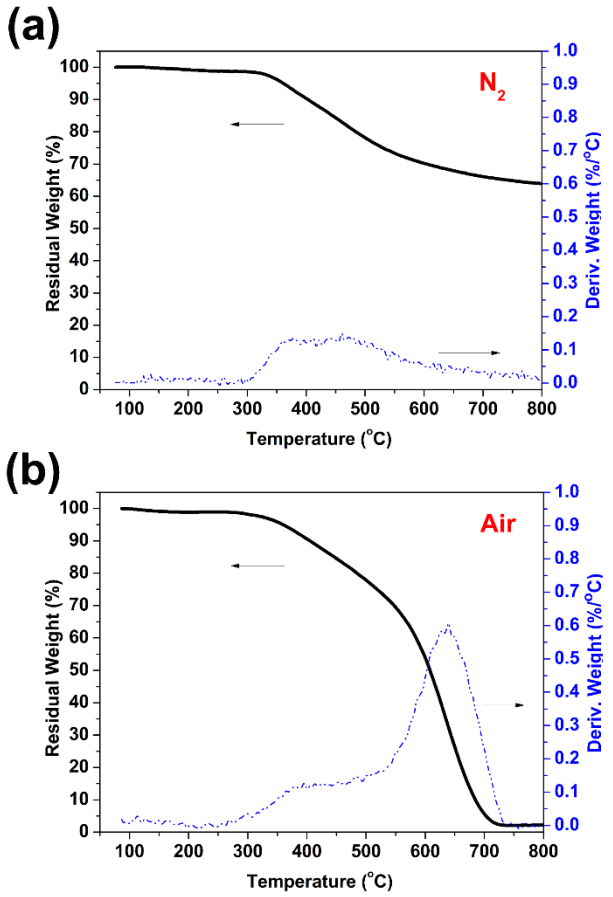


Figure S10. TGA (—) and DTG (····) thermograms of **poly(NAR-fa)** under nitrogen (a) and air (b) atmospheres.

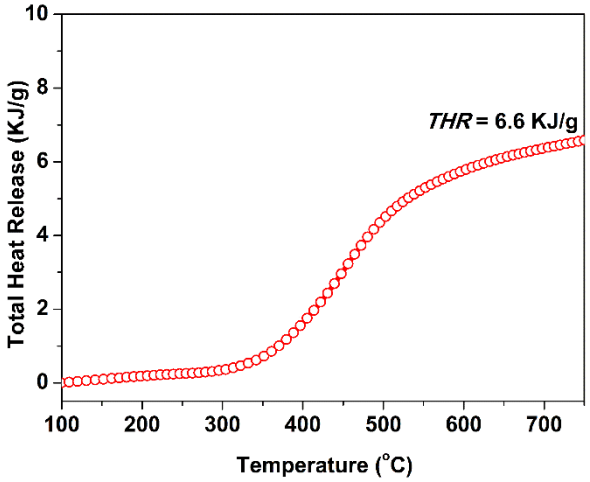


Figure S11. Microscale combustion calorimetric (MCC) analysis of **poly(NAR-fa)**. Plots of the total heat release as a function of the temperature.

Table S1. Thermal and fire related properties of **poly(NAR-fa)**.

Sample	T_g (TMA) (℃)	T_g (DMA) (℃)	N_2			Air			HRC ($Jg^{-1}K^{-1}$)	THR (KJg^{-1})
			T_{d5} (℃)	T_{d10} (℃)	Yc (%)	T_{d5} (℃)	T_{d10} (℃)	Yc (%)		
Poly(NAR-fa)	278	286	361	404	64	360	407	2	31.9	6.6

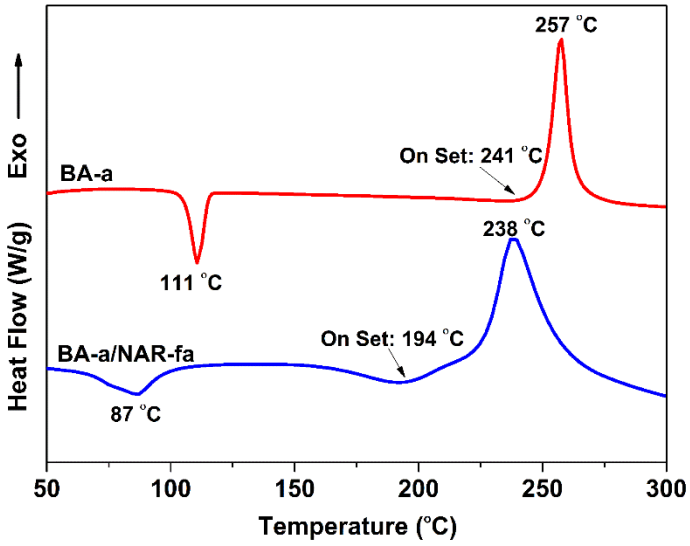


Figure S12. DSC thermograms of benzoxazine resins (BA-a and **BA-a/NAR-fa blend**).

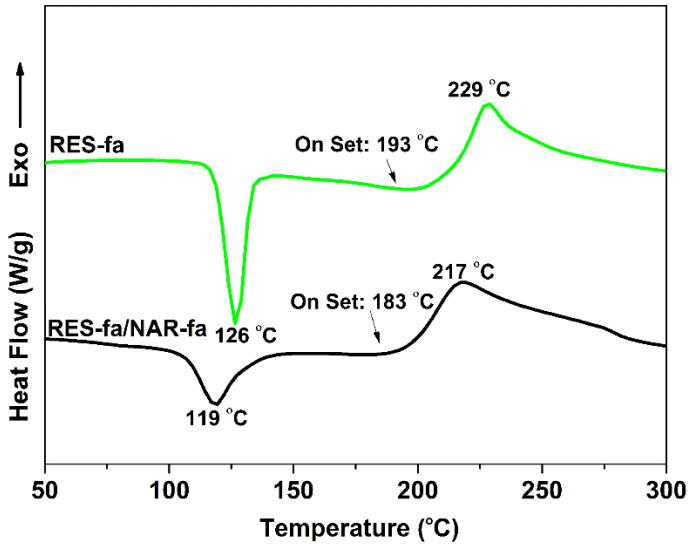


Figure S13. DSC thermograms of benzoxazine resins (RES-fa and **RES-fa/NAR-fa**

blend).

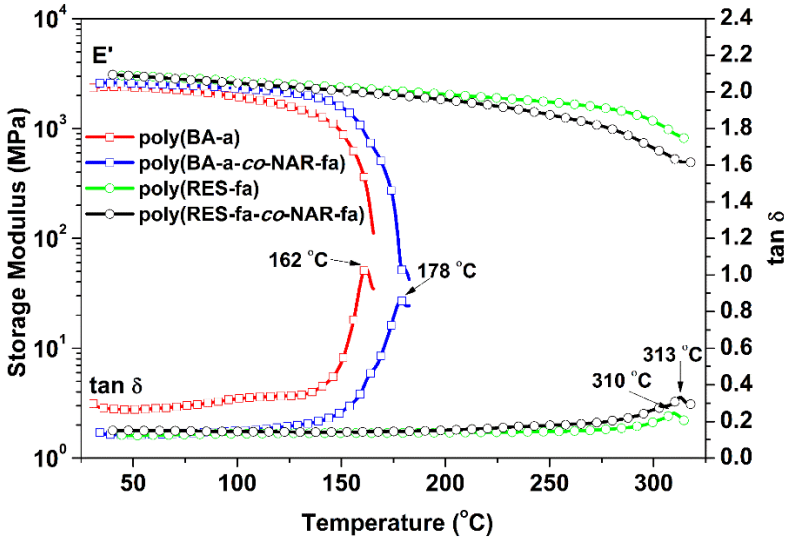


Figure S14. Dynamic mechanical analysis of polybenzoxazines.

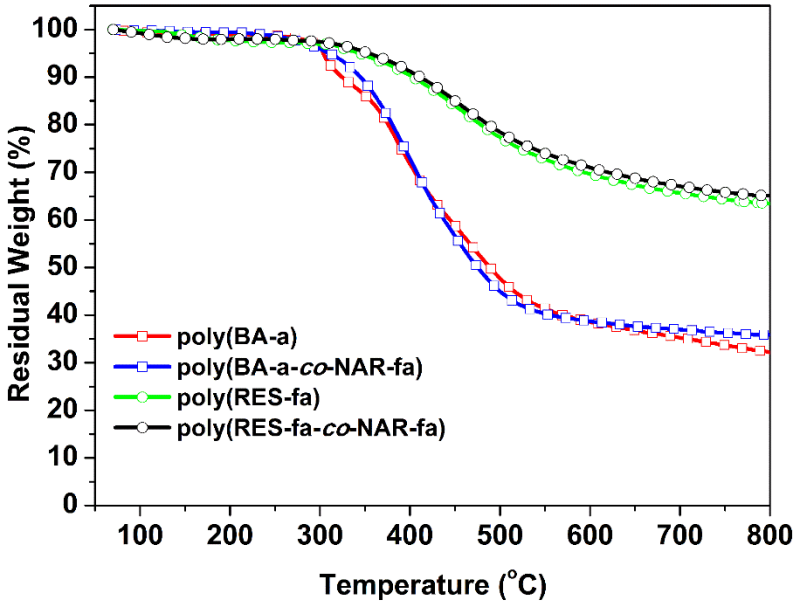


Figure S15. TGA (—) thermograms of polybenzoxazines under nitrogen atmosphere.

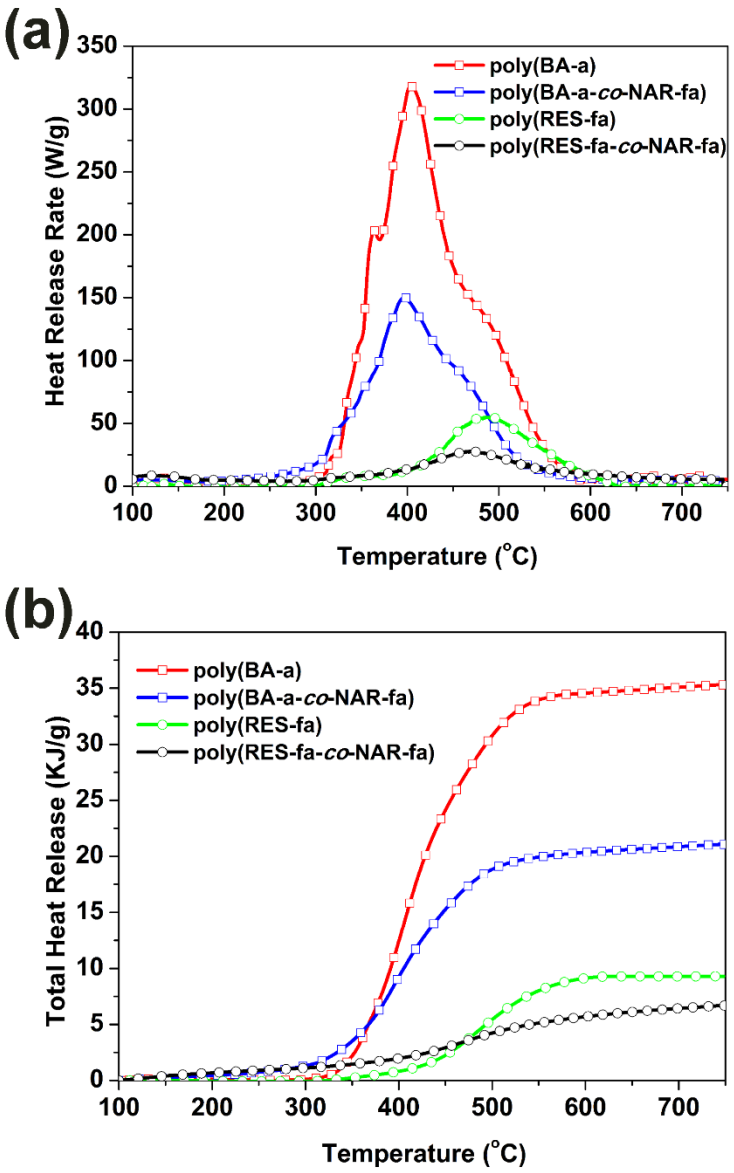


Figure S16. Microscale combustion calorimetric (MCC) analysis of polybenzoxazines. Plots of the heat release rate (a) and total heat release (b) as a function of the temperature.