

Supporting Information

The first observation of 3,1-benzoxazine polymerization for developing high performance thermosets

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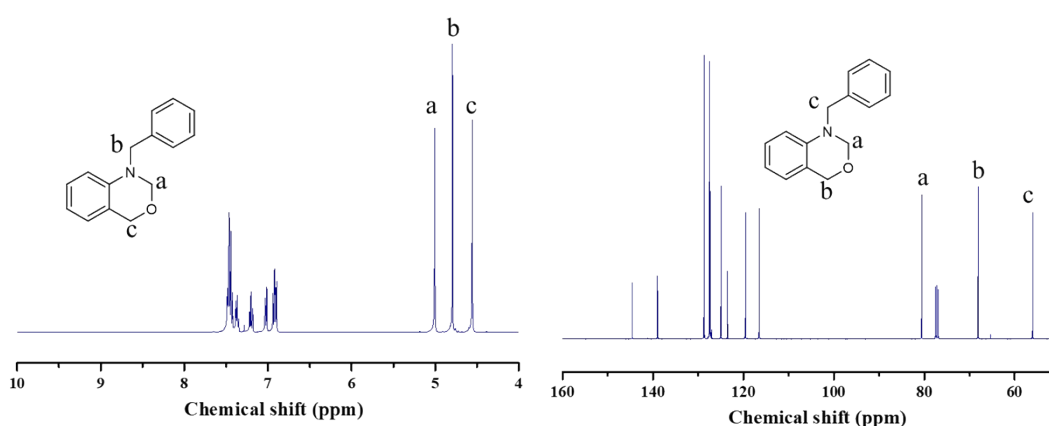


Figure S1 ^1H -NMR spectrum and (left) and ^{13}C -NMR spectrum (right) of 31Bz

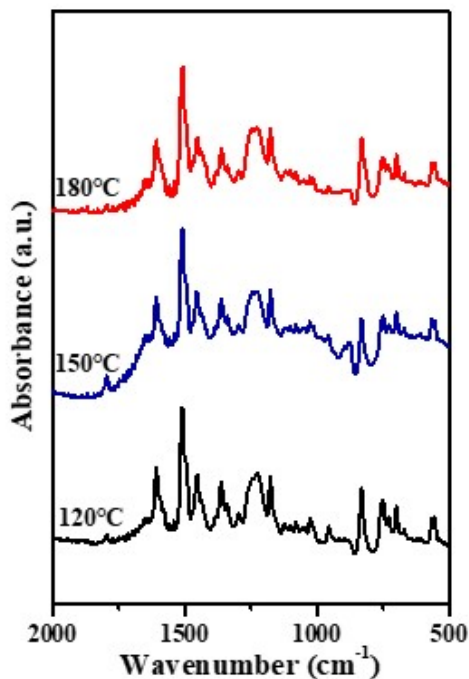


Figure S2 FT-IR spectra of 31Bz with bisphenol A (molar ratio 2:1) after heating at elevated temperatures.

Polymerization kinetics calculation

The apparent activation energy (E_a) of 31HBz polymerization is calculated based on Kissinger method, which assumes that the maximum conversion rate takes place at the temperature of curing peak (T_p):

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{Q_p A R}{E_a}\right) - \left(\frac{E_a}{RT_p}\right)$$

where T_p represents the absolute curing peak temperature (K), β is the heating rate ($^{\circ}\text{C}/\text{min}$), A is the pre-exponential factor and R is the universal gas constant. E_a is calculated from the slope of $\ln(\beta/T_p^2)$ versus $1/T_p$.

Friedman method is used to determine the kinetic model of the polymerization, which can be expressed as:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\beta \frac{d\alpha}{dT} = \ln[Af(\alpha)] - \frac{E_a}{RT}$$

where t is the time, β is the heating rate, $f(\alpha)$ is a function related to α and reaction order. $\ln[Af(\alpha)]$ can be obtained from $\ln(d\alpha/dt)$ and E_a/RT . The activation energy here is selected from the results of Kissinger method.

Reaction order is analyzed based on the Crane equation, which can be expressed as:

$$\frac{d(\ln\beta)}{d(1/T_p)} = - \left[\frac{E_a}{nR} + 2T_p \right] \approx - \frac{E_a}{nR}$$

where n is the reaction order, which can be calculated by linear fitting of $\ln\beta$ versus $1/T_p$. The activation energy here is selected from the results of Kissinger method.

The T_p s of the DSC thermograms are summarized in Table S1:

Table S1 T_p s of the DSC thermograms of 31HBz

Heating rate (β , °C/min)	Curing peak temperature (T_p , °C)
5	212.9
10	227.4
15	235.1
20	244.7

Cartesian coordinates of optimized 31HBz and 31Bz molecular structures

31HBz-O type (O...HO)

C	-2.116478	2.545291	0.202903
C	-1.390832	1.622505	0.938396
C	-1.391716	0.269488	0.578798
C	-2.106791	-0.138749	-0.558079
C	-2.849333	0.800023	-1.273208
C	-2.861302	2.136516	-0.902014
H	-2.109275	3.589316	0.497969
H	-0.832205	1.941201	1.810729
H	-3.406337	0.478695	-2.149751
H	-3.436633	2.856596	-1.473215

C	-2.043381	-1.573665	-1.030378
H	-1.733216	-1.616506	-2.077153
H	-3.030901	-2.053216	-0.954587
O	-1.091895	-2.351048	-0.309560
N	-0.716925	-0.697026	1.345182
C	-1.161499	-2.025009	1.084570
H	-0.533504	-2.746731	1.604984
H	-2.204173	-2.139891	1.407586
C	0.679715	-0.467816	1.745243
H	1.042571	-1.420954	2.142428
H	0.696090	0.236239	2.584097
C	1.638021	0.039808	0.690978
C	2.203086	1.308520	0.837634
C	2.055580	-0.751881	-0.394731
C	3.165956	1.792943	-0.038241
H	1.888816	1.921501	1.678108
C	3.032814	-0.271180	-1.267747
C	3.586072	0.989094	-1.092676
H	3.587852	2.781507	0.105633
H	3.341720	-0.916053	-2.083009
H	4.342799	1.344362	-1.784747
O	1.608083	-2.017533	-0.606016
H	0.635900	-2.083569	-0.529437

31HBz-N type (N...HO)

C	-3.299128	-2.050984	0.511614
C	-1.989042	-1.654442	0.275419

C	-1.698312	-0.317518	-0.021858
C	-2.731223	0.627808	-0.079150
C	-4.047338	0.209112	0.139027
C	-4.335781	-1.117612	0.437585
H	-3.514712	-3.091290	0.737603
H	-1.179165	-2.379186	0.298357
H	-4.852313	0.939810	0.088437
H	-5.362646	-1.425118	0.612318
C	-2.416171	2.075718	-0.377231
H	-2.884546	2.729791	0.365588
H	-2.826617	2.353535	-1.364196
O	-1.029134	2.352283	-0.332342
N	-0.349405	0.073997	-0.297246
C	-0.307872	1.343477	-1.004751
H	0.728798	1.678353	-1.072835
H	-0.713433	1.186959	-2.015269
C	0.538047	0.055135	0.894909
H	0.277727	-0.845265	1.463246
H	0.324545	0.917134	1.542119
C	1.998306	0.020083	0.521379
C	2.934548	0.795135	1.209740
C	2.453185	-0.860133	-0.482757
C	4.298095	0.691759	0.944445
H	2.581845	1.483134	1.975569
C	3.821115	-0.964791	-0.752650
C	4.735162	-0.199178	-0.036281
H	5.009746	1.299458	1.494953

H	4.141444	-1.651422	-1.530179
H	5.795781	-0.290999	-0.254957
O	1.590811	-1.620023	-1.198462
H	0.704407	-1.202373	-1.090241

31Bz

C	-1.577335	2.611934	-0.280921
C	-0.762024	1.517200	-0.535323
C	-1.223071	0.214408	-0.293692
C	-2.516607	0.039364	0.240663
C	-3.313132	1.151265	0.484882
C	-2.861700	2.440160	0.222682
H	-1.197350	3.609561	-0.476021
H	0.243443	1.675982	-0.904972
H	-4.307211	1.002861	0.899493
H	-3.497222	3.295587	0.422152
C	-3.011302	-1.349675	0.561609
H	-3.794646	-1.658066	-0.150166
H	-3.444288	-1.379334	1.564179
O	-1.963306	-2.305342	0.565390
N	-0.447663	-0.910752	-0.548774
C	-1.166800	-2.166966	-0.575280
H	-1.799874	-2.246949	-1.479977
H	-0.446193	-2.986101	-0.568485
C	0.794266	-0.812647	-1.278936
H	0.683454	-0.172307	-2.166998
H	1.024188	-1.813818	-1.661376

C	1.979438	-0.333070	-0.459363
C	3.086178	0.222575	-1.102671
C	2.005089	-0.477223	0.926168
C	4.203672	0.618486	-0.376113
H	3.073276	0.348909	-2.182420
C	3.120901	-0.078170	1.654885
C	4.224042	0.468342	1.007241
H	5.056647	1.050432	-0.889636
H	3.126245	-0.191869	2.734175
H	5.092651	0.781464	1.577090
H	1.137274	-0.894254	1.426280