Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information for : Solvent-free synthesis of a formaldehyde-free benzoxazine monomer: Study of its curing acceleration effect for commercial benzoxazine

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NMR Spectroscopy

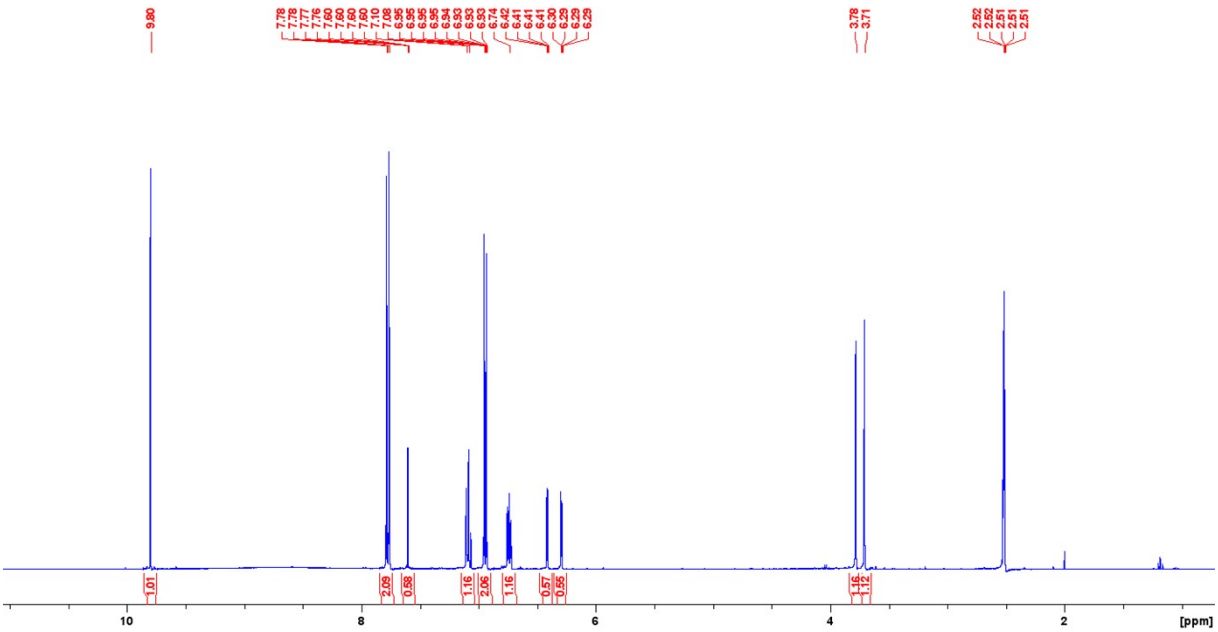

Figure S1 - 1H NMR spectrum of an equimolar mixture of furfurylaminomethylphenol and p-hydroxybenzaldehyde in dmso-d_6

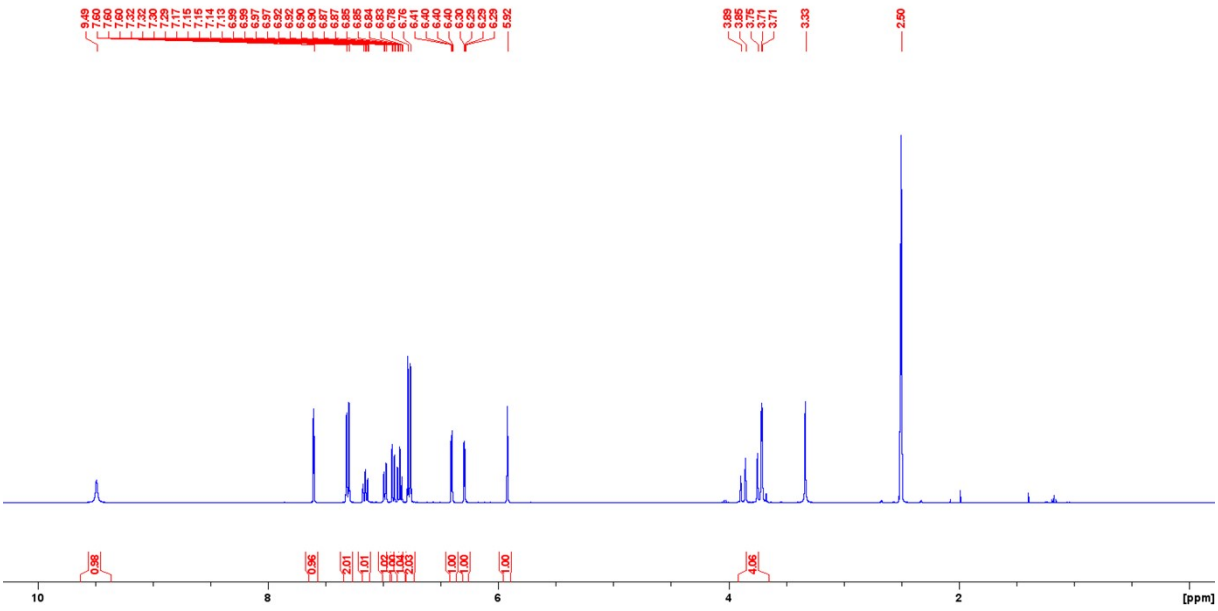

Figure S2 - Full ^{1}H NMR spectrum of Ph-fa[2]PhOH single crystals in dmso-d_6

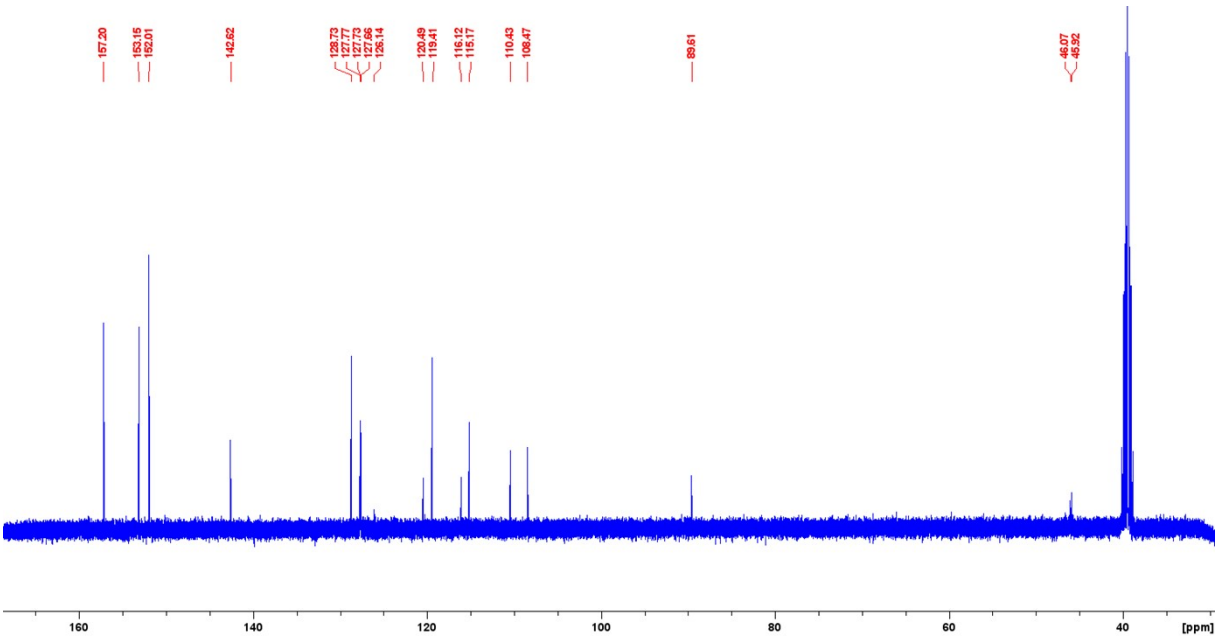

Figure S3 - Full ^{13}C NMR spectra of Ph-fa[2]PhOH in dmso-d_6

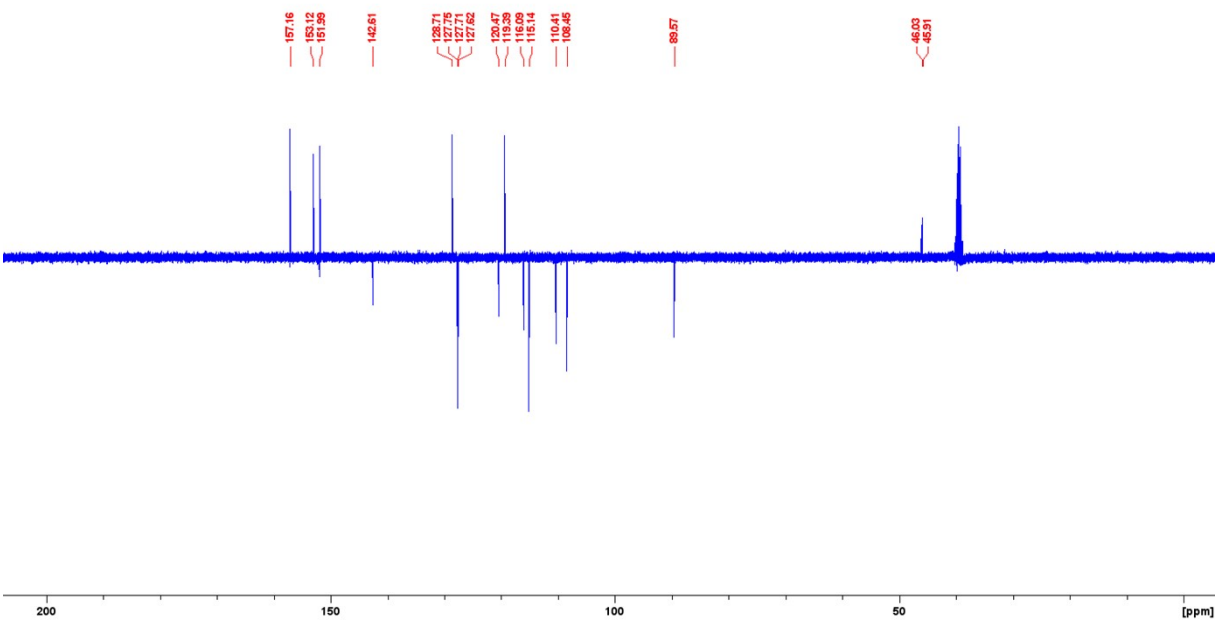

Figure S4 - Full ^{13}C NMR spectrum of an APT experiment on Ph-fa[2]PhOH in dmso-d_6 (showing secondary and quaternary ^{13}C positive (up) and primary or tertiary ^{13}C negative (down))

FTIR spectroscopy

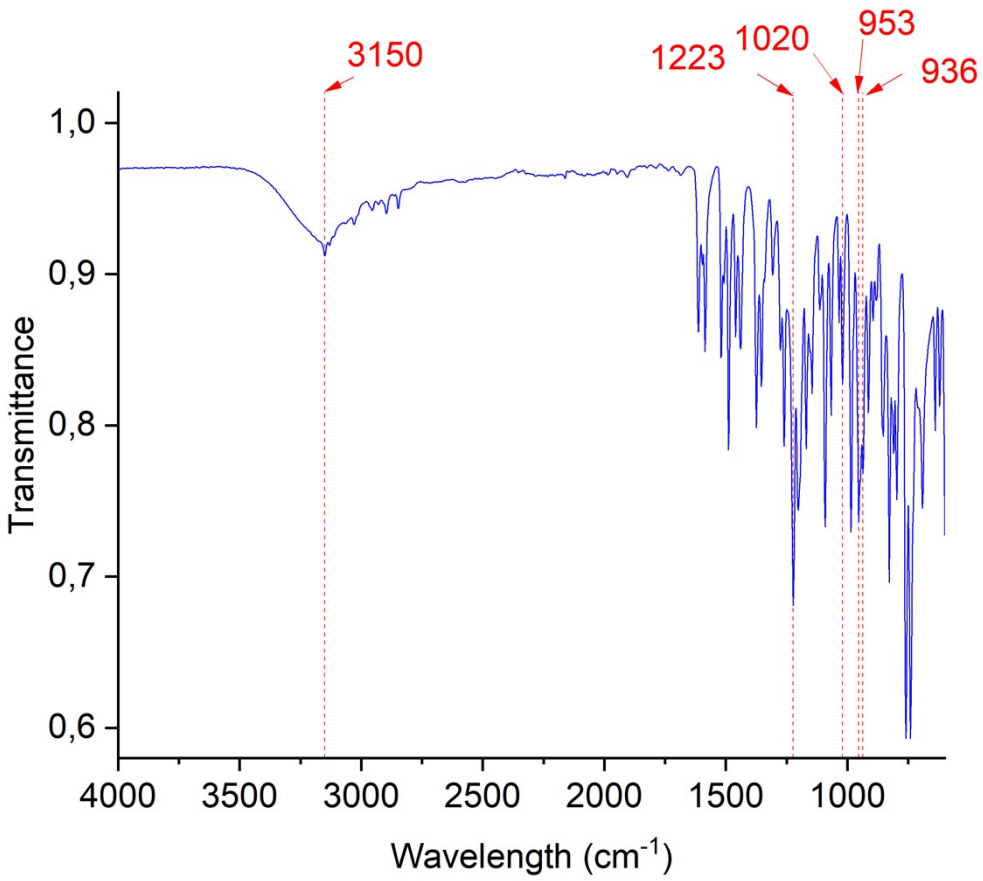

Figure S5 - Full IR spectrum of Ph-fa[2]PhOH

Single crystals X-ray Diffraction

Figure S6 - Picture of single crystals of Ph-fa[2]PhOH

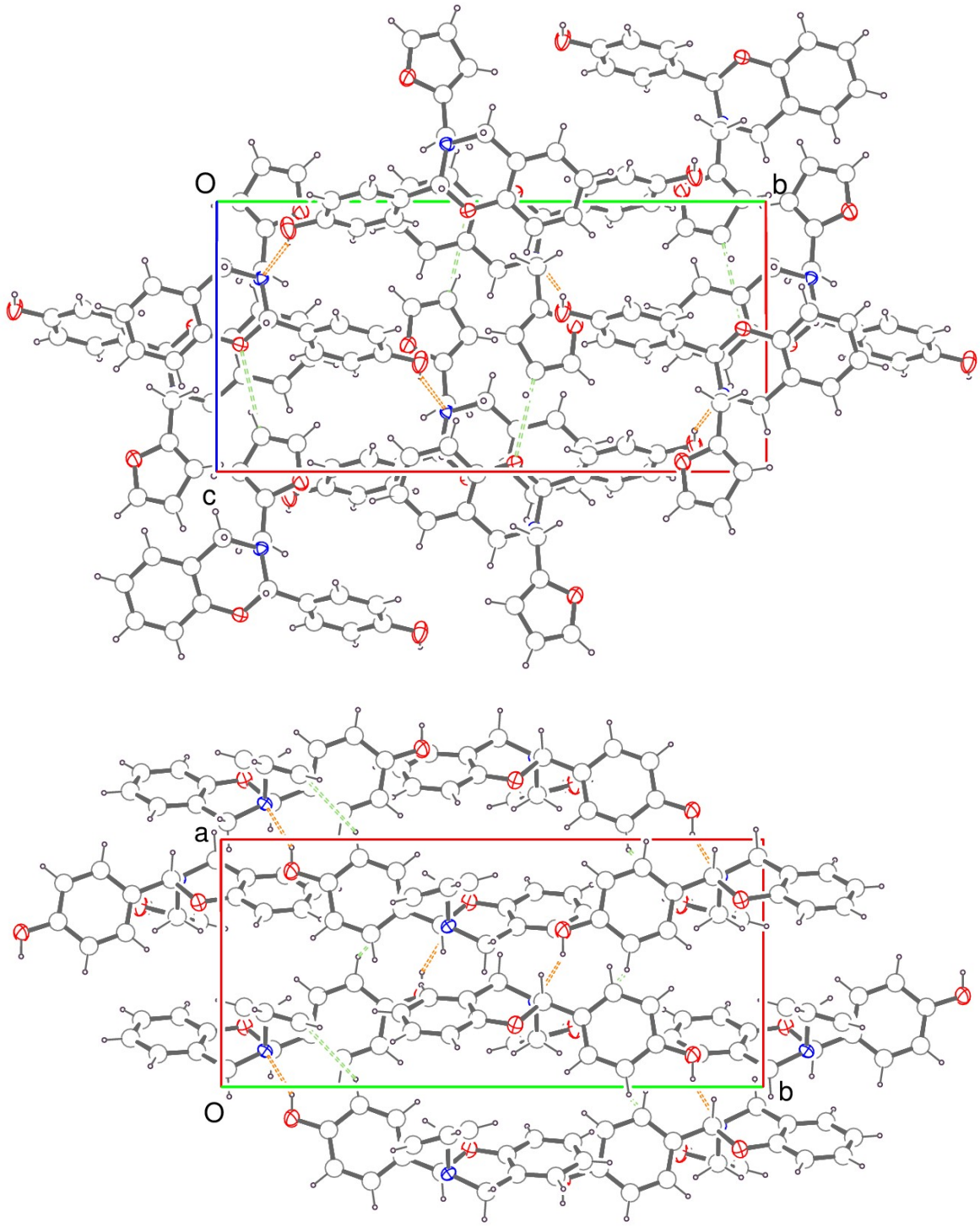

Figure S7 -The molecular packing in the crystal, viewed along the a-axis (up) and c-axis (down). The intermolecular interactions are drawn as dashed lines, green for the 3.267 Å weak O1···C12 interactions and orange for the O3···N hydrogen bonds of 2.821Å

Table S1 - Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å² × 10^3) for $C_{19}H_{17}NO_3$. U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atoms	*x*	*y*	*z*	U(eq)
N	3519(1)	5804(1)	2141(1)	25(1)
C(4)	2241(2)	3517(1)	-534(2)	45(1)
C(5)	2994(2)	3318(1)	852(2)	46(1)
C(7)	3534(1)	4541(1)	1495(1)	30(1)
C(8)	4259(1)	5110(1)	2545(1)	29(1)
C(9)	1958(1)	5828(1)	2427(1)	29(1)
C(10)	2038(1)	5880(1)	3982(1)	27(1)
C(11)	2389(2)	6454(1)	6016(1)	42(1)
C(12)	2000(2)	5804(1)	6283(1)	43(1)
C(13)	1774(2)	5426(1)	4962(1)	40(1)
C(14)	2830(1)	6657(1)	127(1)	26(1)
C(15)	1284(1)	6772(1)	-587(1)	29(1)
C(16)	737(1)	7448(1)	-960(1)	31(1)
C(17)	1733(1)	8021(1)	-640(1)	33(1)
C(18)	3285(1)	7913(1)	56(2)	39(1)
C(19)	3815(1)	7236(1)	430(1)	34(1)
C(6)	3633(1)	3827(1)	1857(2)	38(1)
O(1)	2510(1)	5424(1)	-314(1)	32(1)
C(1)	3458(1)	5936(1)	629(1)	26(1)
O(2)	2429(1)	6525(1)	4609(1)	40(1)
C(2)	2742(1)	4731(1)	105(1)	29(1)
O(3)	1266(1)	8698(1)	-973(1)	47(1)
C(3)	2103(1)	4222(1)	-919(2)	37(1)

Table S2 - Bond lengths (Å) for C_{19} H_{17} N O_3.

Bond	Bond length (Å)
N-C(1)	1.4619(13)
N-C(8)	1.4800(13)
N-C(9)	1.4837(14)
C(4)-C(3)	1.3830(19)
C(4)-C(5)	1.386(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.3828(19)
C(5)-H(5)	0.9500
C(7)-C(2)	1.3932(16)
C(7)-C(6)	1.3954(16)
C(7)-C(8)	1.5069(15)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.4812(15)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(13)	1.3394(16)
C(10)-O(2)	1.3679(13)
C(11)-C(12)	1.322(2)
C(11)-O(2)	1.3677(15)
C(11)-H(11)	0.9500
C(12)-C(13)	1.4279(18)

Bond	Bond length (Å)
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500
C(14)-C(19)	1.3898(16)
C(14)-C(15)	1.3947(15)
C(14)-C(1)	1.5091(14)
C(15)-C(16)	1.3866(15)
C(15)-H(15)	0.9500
C(16)-C(17)	1.3868(16)
C(16)-H(16)	0.9500
C(17)-O(3)	1.3625(14)
C(17)-C(18)	1.3936(17)
C(18)-C(19)	1.3842(17)
C(18)-H(18)	0.9500
C(19)-H(19)	0.9500
C(6)-H(6)	0.9500
O(1)-C(2)	1.3744(14)
O(1)-C(1)	1.4479(13)
C(1)-H(1)	1.0000
C(2)-C(3)	1.3945(16)
O(3)-H(1O)	0.88(2)
C(3)-H(3)	0.9500

Table S3 - Bond angles (°) for $C_{19}H_{17}NO_3$.

Bond	Angle (°)	Bond	Angle (°)	Bond	Angle (°)	Bond	Angle (°)
C(1)-N-C(8)	108.46(8)	**C(10)-C(9)-N**	112.19(9)	**C(19)-C(14)-C(15)**	118.33(10)	**C(5)-C(6)-C(7)**	120.88(13)
C(1)-N-C(9)	112.02(8)	**C(10)-C(9)-H(9A)**	109.2	**C(19)-C(14)-C(1)**	118.86(9)	**C(5)-C(6)-H(6)**	119.6
C(8)-N-C(9)	110.82(8)	**N-C(9)-H(9A)**	109.2	**C(15)-C(14)-C(1)**	122.77(10)	**C(7)-C(6)-H(6)**	119.6
C(3)-C(4)-C(5)	120.60(12)	**C(10)-C(9)-H(9B)**	109.2	**C(16)-C(15)-C(14)**	120.79(10)	**C(2)-O(1)-C(1)**	115.88(8)
C(3)-C(4)-H(4)	119.7	**N-C(9)-H(9B)**	109.2	**C(16)-C(15)-H(15)**	119.6	**O(1)-C(1)-N**	112.20(9)
C(5)-C(4)-H(4)	119.7	**H(9A)-C(9)-H(9B)**	107.9	**C(14)-C(15)-H(15)**	119.6	**O(1)-C(1)-C(14)**	107.15(8)
C(6)-C(5)-C(4)	119.85(12)	**C(13)-C(10)-O(2)**	109.49(10)	**C(15)-C(16)-C(17)**	120.15(10)	**N-C(1)-C(14)**	113.03(8)
C(6)-C(5)-H(5)	120.1	**C(13)-C(10)-C(9)**	133.90(11)	**C(15)-C(16)-H(16)**	119.9	**O(1)-C(1)-H(1)**	108.1
C(4)-C(5)-H(5)	120.1	**O(2)-C(10)-C(9)**	116.59(9)	**C(17)-C(16)-H(16)**	119.9	**N-C(1)-H(1)**	108.1
C(2)-C(7)-C(6)	118.34(11)	**C(12)-C(11)-O(2)**	110.83(11)	**O(3)-C(17)-C(16)**	122.95(10)	**C(14)-C(1)-H(1)**	108.1
C(2)-C(7)-C(8)	119.21(10)	**C(12)-C(11)-H(11)**	124.6	**O(3)-C(17)-C(18)**	117.36(11)	**C(11)-O(2)-C(10)**	106.39(9)
C(6)-C(7)-C(8)	122.45(11)	**O(2)-C(11)-H(11)**	124.6	**C(16)-C(17)-C(18)**	119.69(11)	**O(1)-C(2)-C(7)**	122.02(10)
N-C(8)-C(7)	111.79(9)	**C(11)-C(12)-C(13)**	106.29(11)	**C(19)-C(18)-C(17)**	119.60(11)	**O(1)-C(2)-C(3)**	116.75(11)
N-C(8)-H(8A)	109.3	**C(11)-C(12)-H(12)**	126.9	**C(19)-C(18)-H(18)**	120.2	**C(7)-C(2)-C(3)**	121.21(11)
C(7)-C(8)-H(8A)	109.3	**C(13)-C(12)-H(12)**	126.9	**C(17)-C(18)-H(18)**	120.2	**C(17)-O(3)-H(1O)**	109.5(13)
N-C(8)-H(8B)	109.3	**C(10)-C(13)-C(12)**	106.99(12)	**C(18)-C(19)-C(14)**	121.42(10)	**C(4)-C(3)-C(2)**	119.10(13)
C(7)-C(8)-H(8B)	109.3	**C(10)-C(13)-H(13)**	126.5	**C(18)-C(19)-H(19)**	119.3	**C(4)-C(3)-H(3)**	120.5
H(8A)-C(8)-H(8B)	107.9	**C(12)-C(13)-H(13)**	126.5	**C(14)-C(19)-H(19)**	119.3	**C(2)-C(3)-H(3)**	120.5

Table 4 - Anisotropic displacement parameters ($Å^2 \times 10^3$)for $C_{19}H_{17}NO_3$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}]$

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N	24(1)	27(1)	23(1)	2(1)	4(1)	4(1)
C(4)	32(1)	36(1)	67(1)	-17(1)	9(1)	-5(1)
C(5)	37(1)	28(1)	74(1)	-3(1)	13(1)	-2(1)
C(7)	24(1)	28(1)	36(1)	-1(1)	8(1)	2(1)
C(8)	28(1)	27(1)	30(1)	2(1)	3(1)	5(1)
C(9)	25(1)	37(1)	25(1)	3(1)	6(1)	5(1)
C(10)	27(1)	28(1)	27(1)	1(1)	7(1)	4(1)
C(11)	47(1)	48(1)	31(1)	-11(1)	10(1)	5(1)
C(12)	53(1)	52(1)	26(1)	7(1)	12(1)	14(1)
C(13)	56(1)	33(1)	34(1)	5(1)	18(1)	1(1)
C(14)	28(1)	31(1)	21(1)	2(1)	7(1)	3(1)
C(15)	28(1)	31(1)	26(1)	1(1)	4(1)	-2(1)
C(16)	26(1)	35(1)	29(1)	5(1)	1(1)	2(1)
C(17)	34(1)	30(1)	33(1)	5(1)	2(1)	2(1)
C(18)	32(1)	32(1)	47(1)	5(1)	-2(1)	-4(1)
C(19)	26(1)	37(1)	34(1)	5(1)	1(1)	1(1)
C(6)	31(1)	30(1)	53(1)	5(1)	9(1)	2(1)
O(1)	39(1)	30(1)	24(1)	-2(1)	3(1)	2(1)
C(1)	26(1)	30(1)	24(1)	0(1)	6(1)	2(1)
O(2)	56(1)	30(1)	38(1)	-4(1)	20(1)	-2(1)
C(2)	25(1)	30(1)	34(1)	-4(1)	9(1)	2(1)
O(3)	39(1)	29(1)	60(1)	9(1)	-9(1)	1(1)
C(3)	28(1)	40(1)	43(1)	-11(1)	7(1)	-1(1)

DSC

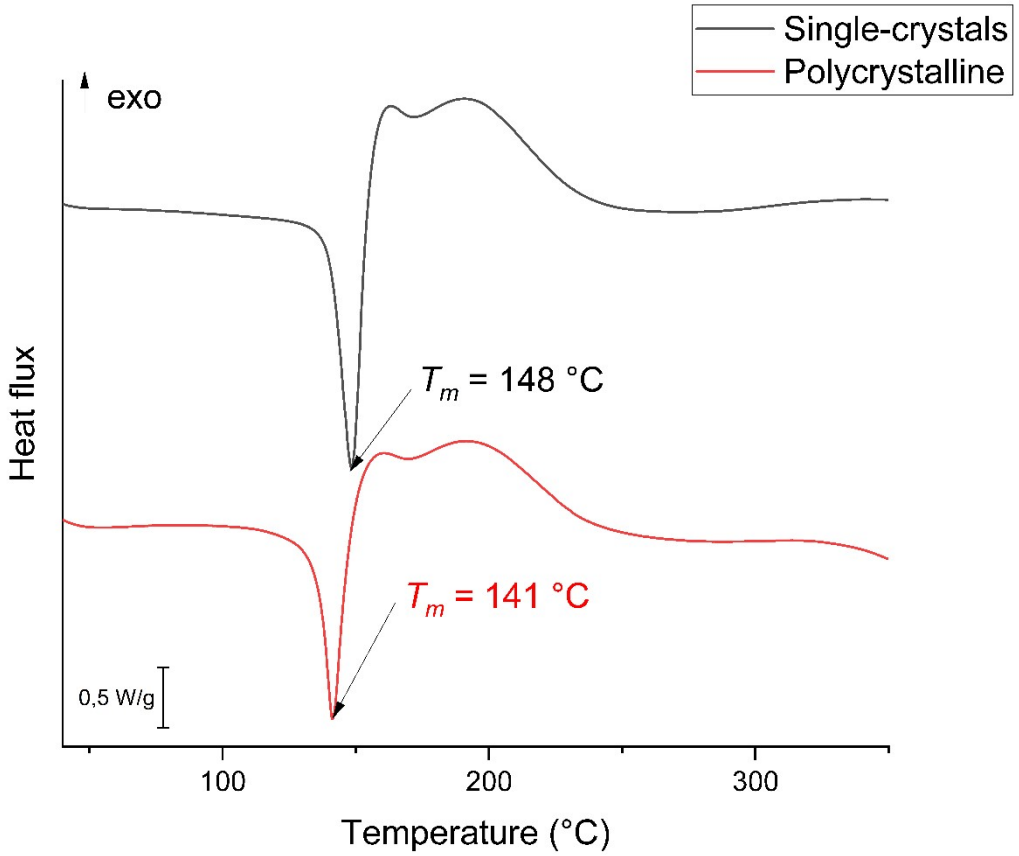

Figure S8 - DSC thermograms of Ph-fa[2]PhOH at 10 °C·min^{-1}. Upper thermogram corresponds to single-crystals, bottom thermogram corresponds to polycrystalline sample.

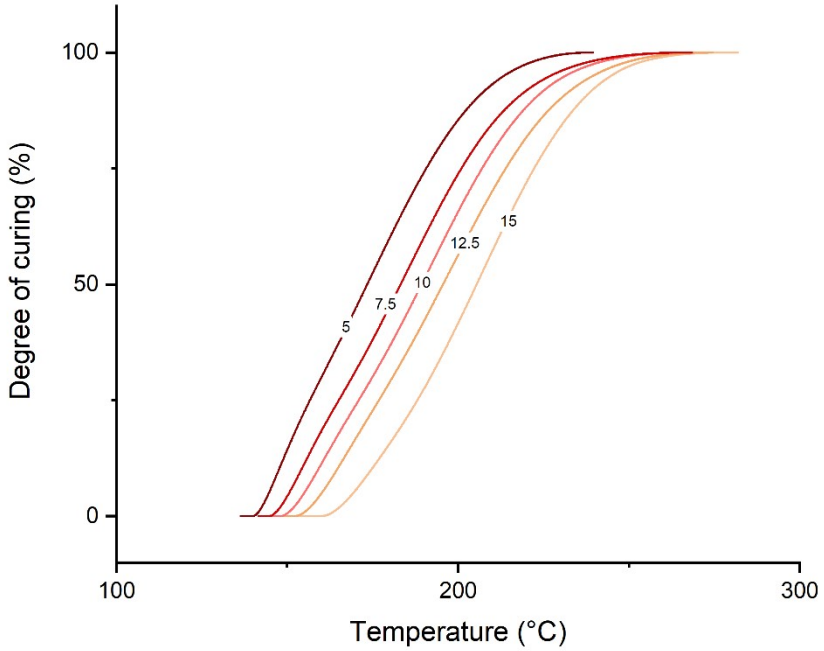

Figure S9 - DSC integrals of Ph-fa[2]PhOH at different heating rates

Rheology

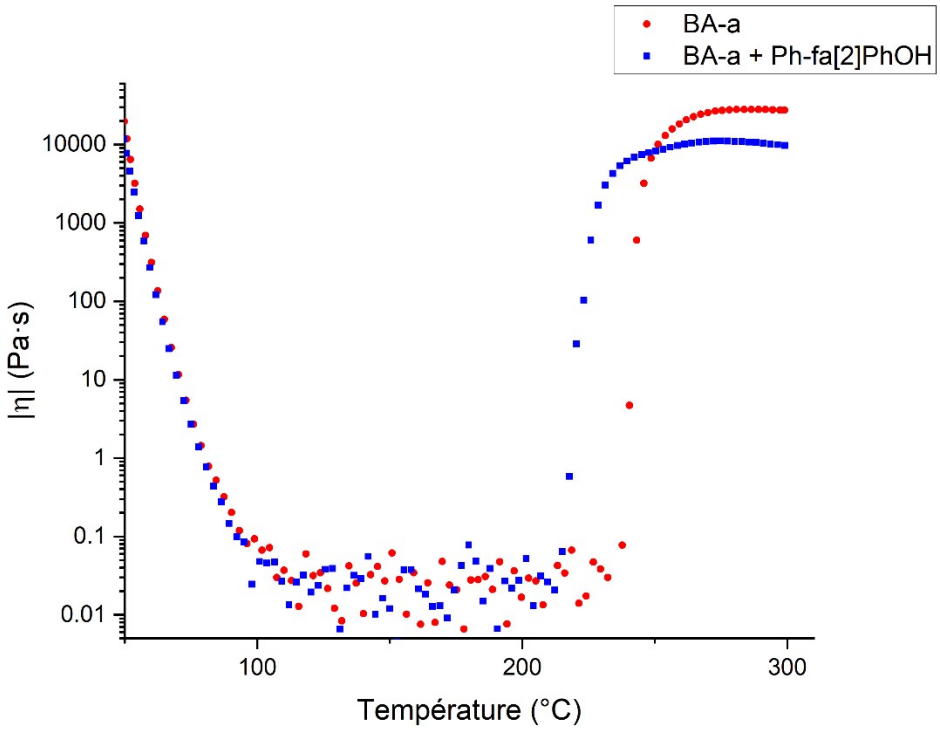

Figure S10 - Complex viscosity of both formulation followed at 10°C·min^{-1}

Samples pictures

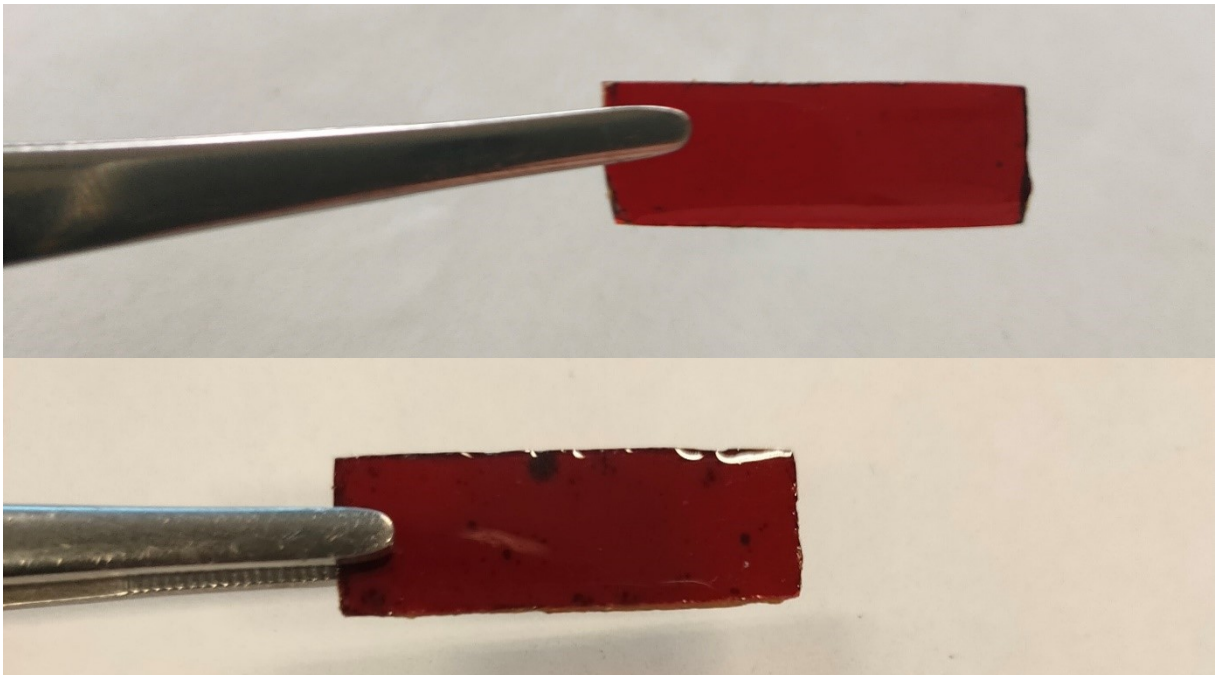

Figure S11 - Pictures of fully cured BA-a (up) and BA-a + 10 wt % Ph-fa[2]PhOH (down)

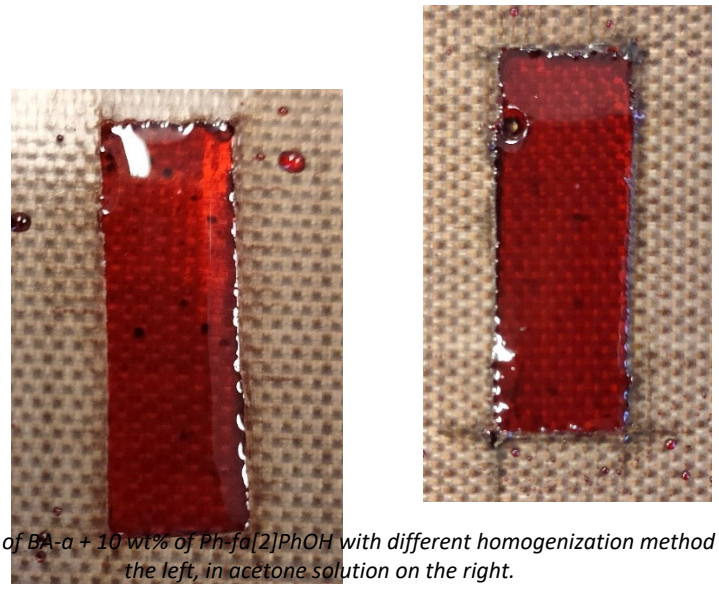

Figure S12 – Cured samples of BA-a + 10 wt% of Ph-fa[2]PhOH with different homogenization method : in molten state on the left, in acetone solution on the right.