Synthesis of Resins Using Epoxies and Humins as Building Blocks: A Mechanistic Study Based on in-situ FT-IR and NMR Spectroscopies

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CONTENTS OF THE SUPPORTING INFORMATION

1. Complementary figures for FT-IR spectroscopy investigations

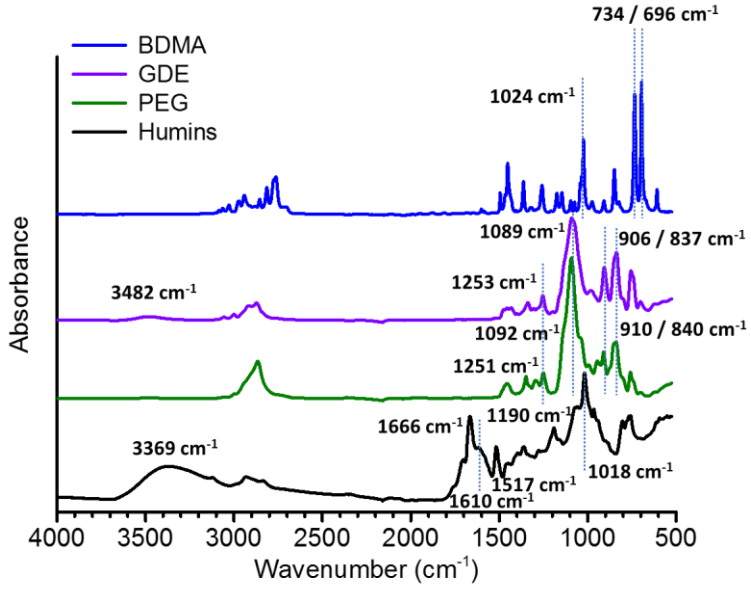

Figure S1. FT-IR spectra of the used catalyst (BDMA) and raw materials: GDE, PEGDE and humins.

Table S1. Assignment of major bands on FT-IR spectra of humins.

Wavenumber (cm^{-1})	Assignment
3369	O-H stretching vibration of associated -OH by hydrogen bonding
3120	-(C=**C)-H** asymmetric/symmetric stretching vibration
2930	C-H (-CH_2-) asymmetric stretching vibration in aliphatic methylene units
2837	C-H (-CH_2-) symmetric stretching vibration in aliphatic methylene units
1702	-C=O stretching vibration of acids, esters and conjugated carbonyl groups
1666	-C=O stretching vibration of aldehyde groups
1617	-C=C- stretching vibration conjugated to -C=O
1580-1500	-C=C- stretching vibration in furan rings
1517	-C=C- stretching vibration in furan rings linked to aldehyde groups
1490-1410	C-H asymmetric bending deformation in -CH_3; C-H asymmetric and symmetric bending deformation in -CH_2-
1360	C-H symmetric bending deformation in -O-CH_3
1190	-C-C- asymmetric stretching vibration in furan rings
1018	-C-O- stretching vibration in furan rings
804	-(C=**C)-H** wagging out-of-plane in furan rings (bending)
768	-(C=**C)-H** wagging out-of-plane in furan rings (bending)

Table S2. Assignments of major bands on FT-IR spectra of GDE, PEGDE and BDMA.

Wavenumber (cm^{-1})	Assignment	Compound
3482	O-H stretching vibration	GDE
3100-3000	C-H stretching vibration (aromatic)	BDMA
3056	C-H stretching vibration (-CH-); epoxy group	PEGDE, GDE
3000	C-H stretching vibration (-CH-); epoxy group	GDE
3000-2700	C-H stretching vibration (aliphatic)	PEGDE, GDE, BDMA
2993	C-H stretching vibration (-CH-); epoxy group	PEGDE
1490-1410	C-H asymmetric and symmetric bending deformation in $-CH_2-$	PEGDE, GDE
1253	C-O-C symmetric stretching vibration of oxirane group; epoxy group	GDE
1251	C-O-C symmetric stretching vibration of oxirane group; epoxy group	PEGDE
1092	C-O-C asymmetric stretching vibration; ether linkage	PEGDE
1089	C-O-C asymmetric stretching vibration; ether linkage	GDE
1024	C-N stretching vibration; aliphatic tertiary amine	BDMA
910	C-O-C asymmetric stretching vibration of oxirane group; epoxy group	PEGDE
906	C-O-C asymmetric stretching vibration of oxirane group; epoxy group	GDE
840	C-O-C bending deformation of oxirane group; epoxy group	PEGDE
837	C-O-C bending deformation of oxirane group; epoxy group	GDE
758	C-H wagging out-of-plane in epoxy ring (bending)	PEGDE
755	C-H wagging out-of-plane in epoxy ring (bending)	GDE
734	C-H out-of-plane bending deformation in the aromatic ring	BDMA
696	C-H out-of-plane bending deformation in the aromatic ring	BDMA

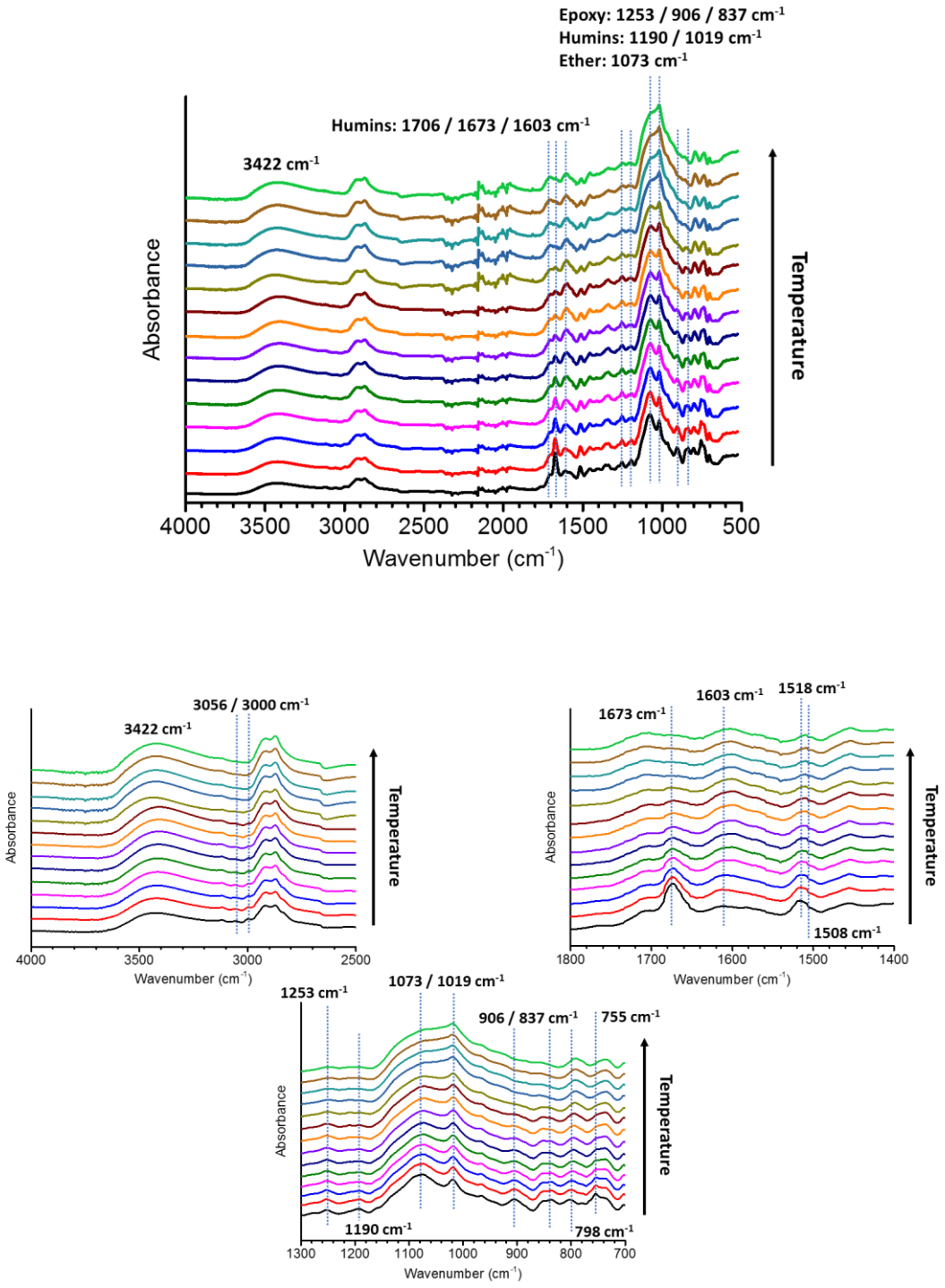

Figure S2. FT-IR spectra evolution during the polymerization of HG40B5.

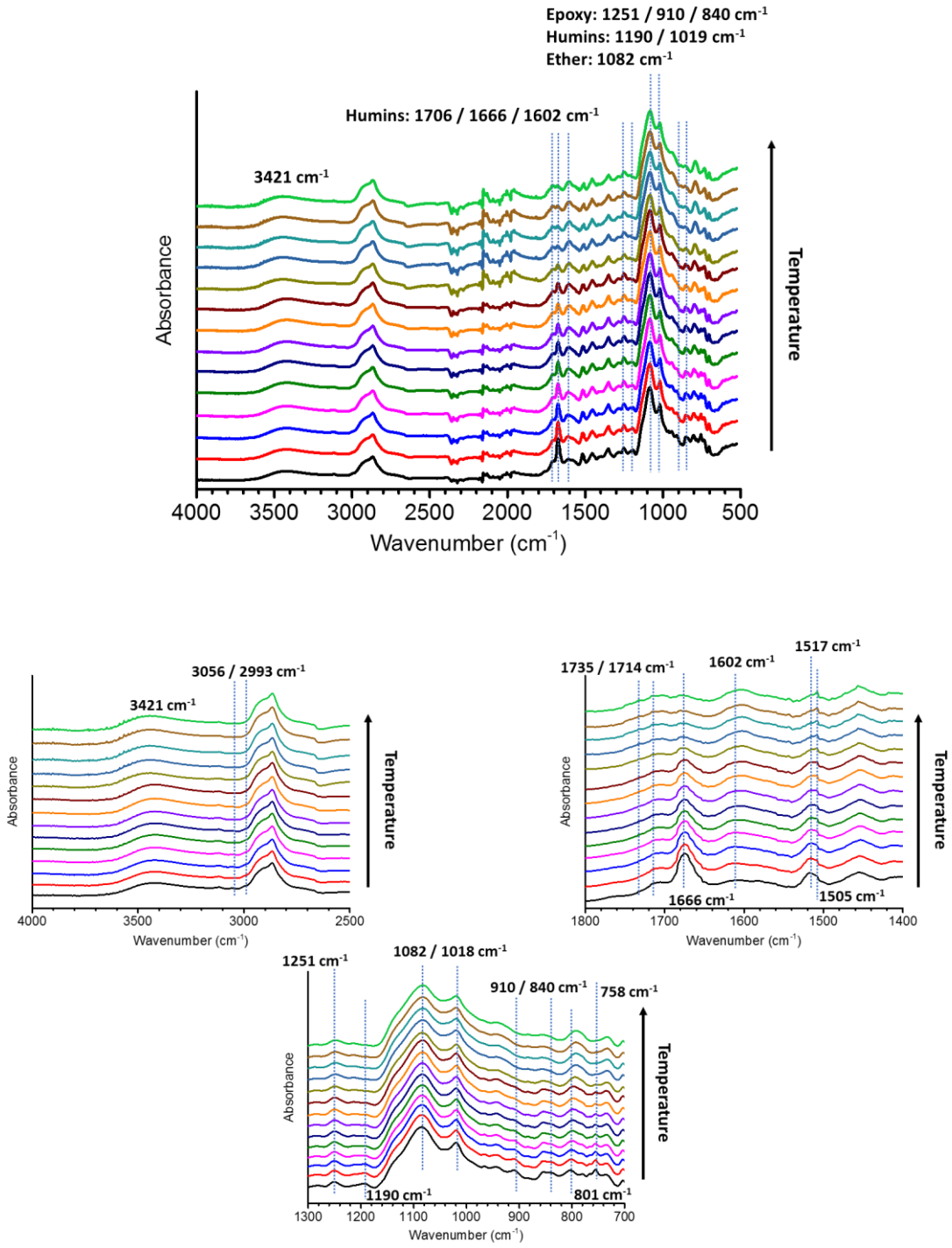

Figure S3. FT-IR spectra evolution during the polymerization of HP40B5.

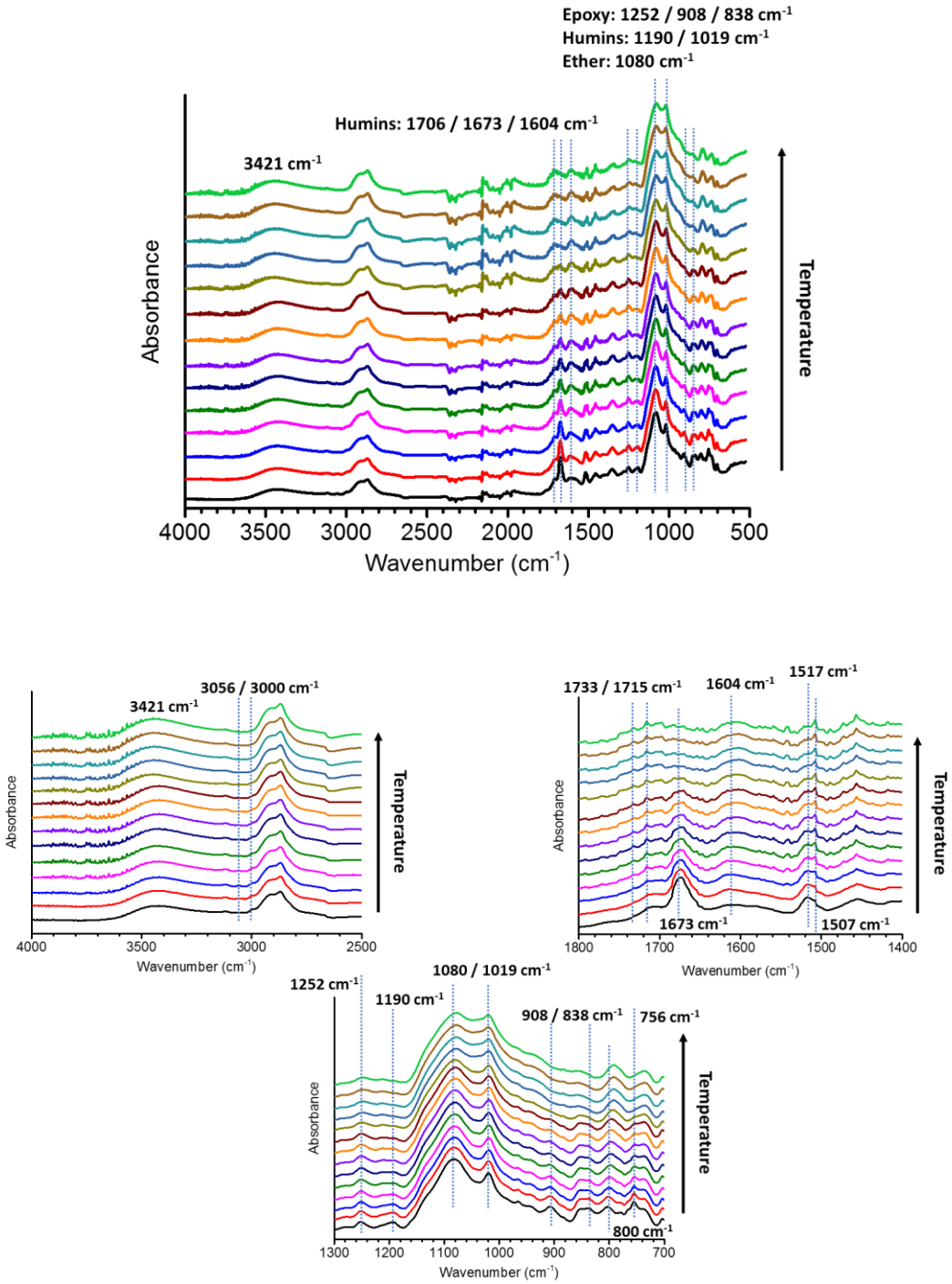

Figure S4. FT-IR spectra evolution during the polymerization of HP20G20B5.

2. Complementary figures for NMR investigations

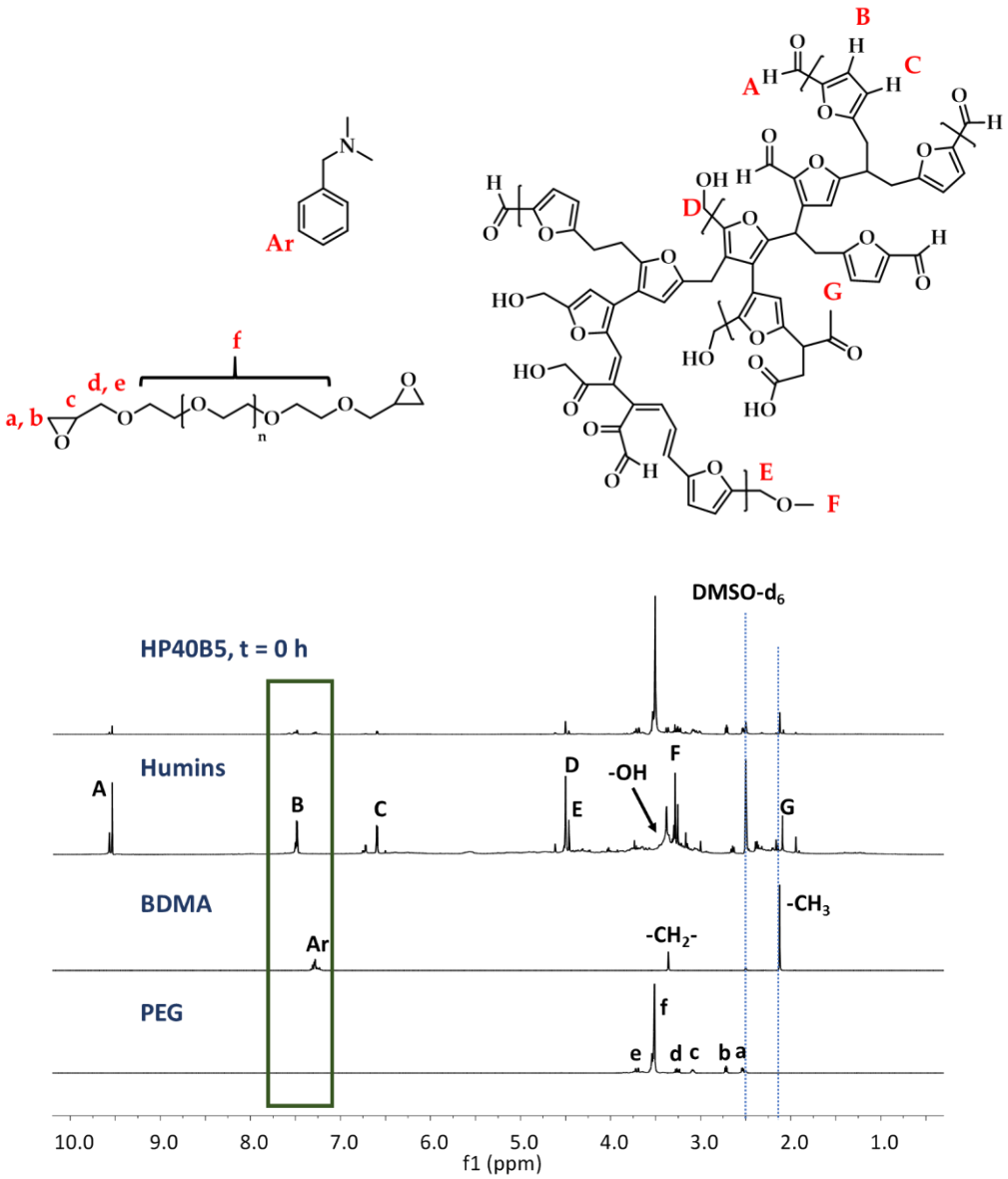

Figure S5. ^{1}H NMR spectra of PEGDE, BDMA, humins and HP40B5 at t = 0.

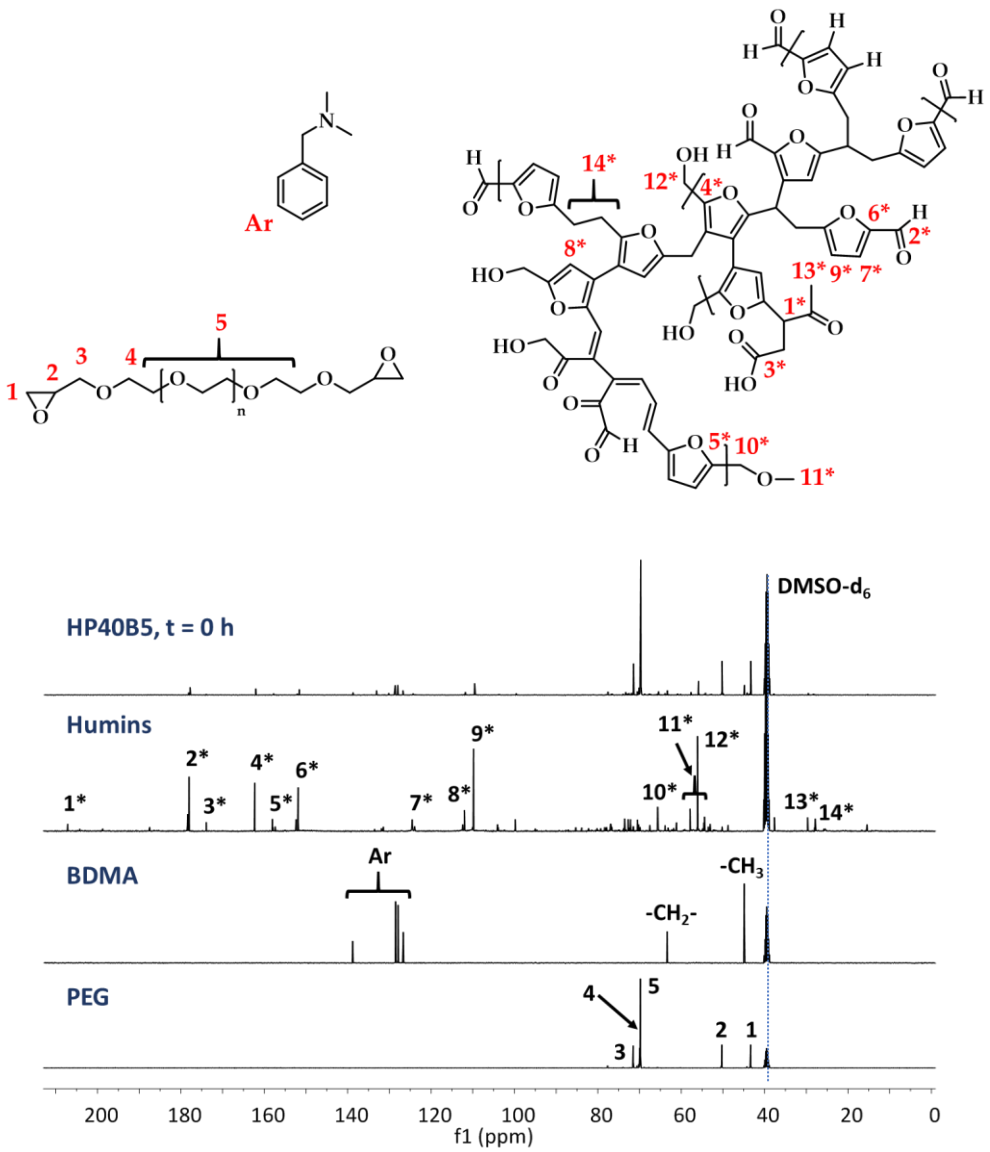

Figure S6. ^{13}C NMR spectra of PEGDE, BDMA, humins and HP40B5 at t = 0.

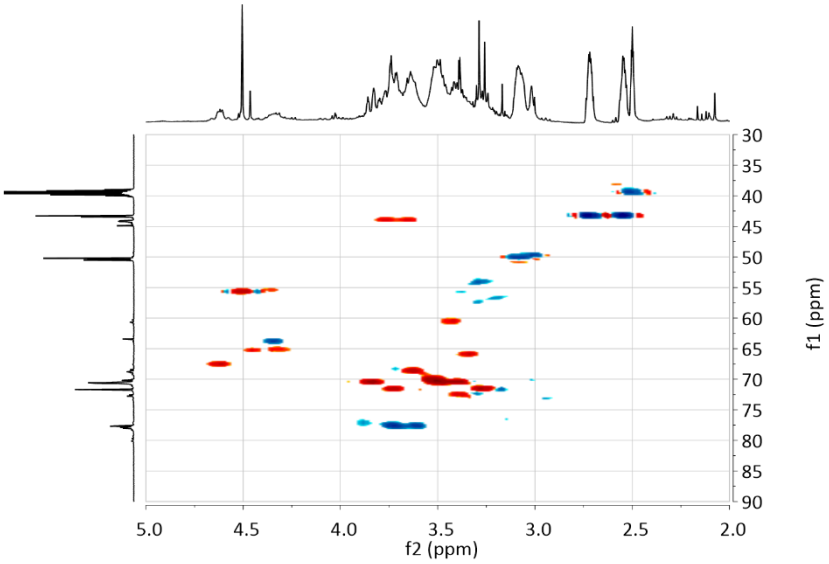

Figure S7. HSQC NMR spectra of HG40B5 at t = 0. In the spectra, the blue signals correspond to -CH- and -CH_3 signals, while the red ones correspond to -CH_2- signals.

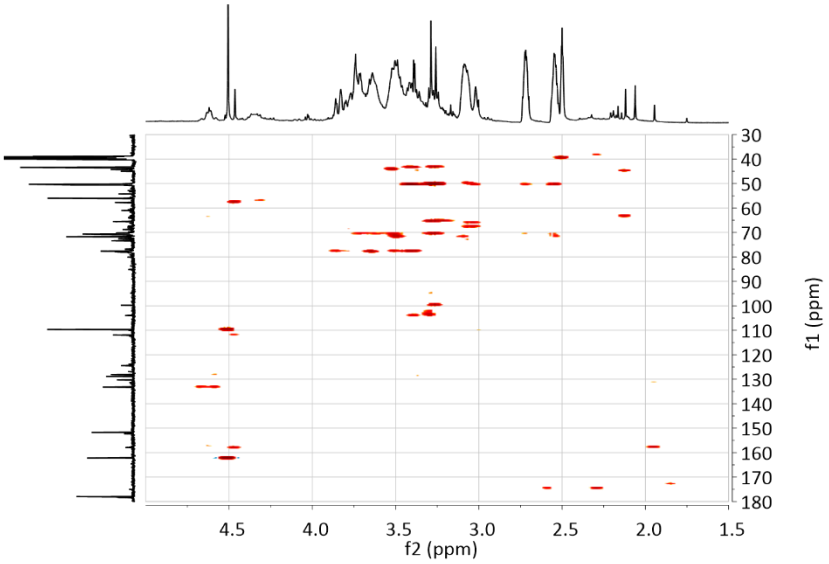

Figure S8. HMBC NMR spectra of HG40B5 at t = 0 h.

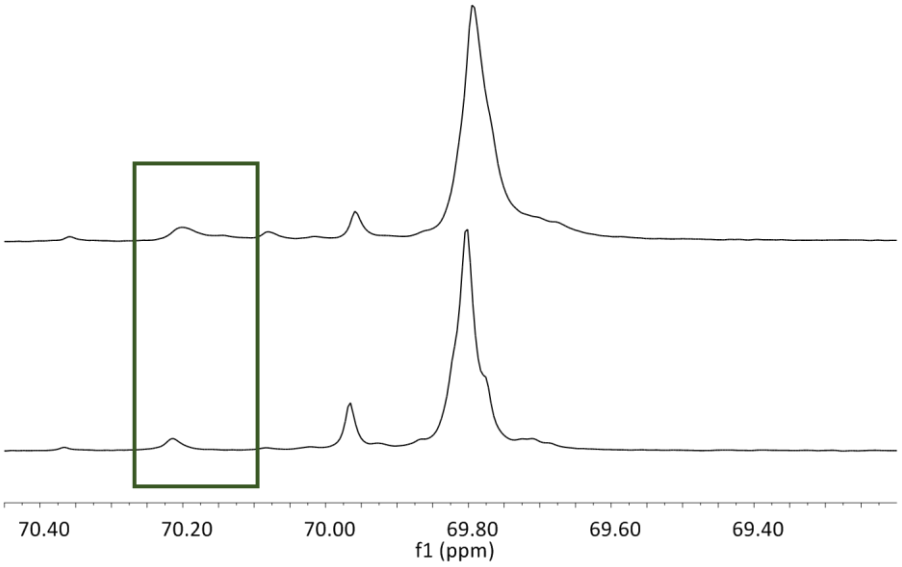

Figure S9. ^{13}C NMR spectra of HP40B5 at t = 0 h and t = 6 h.

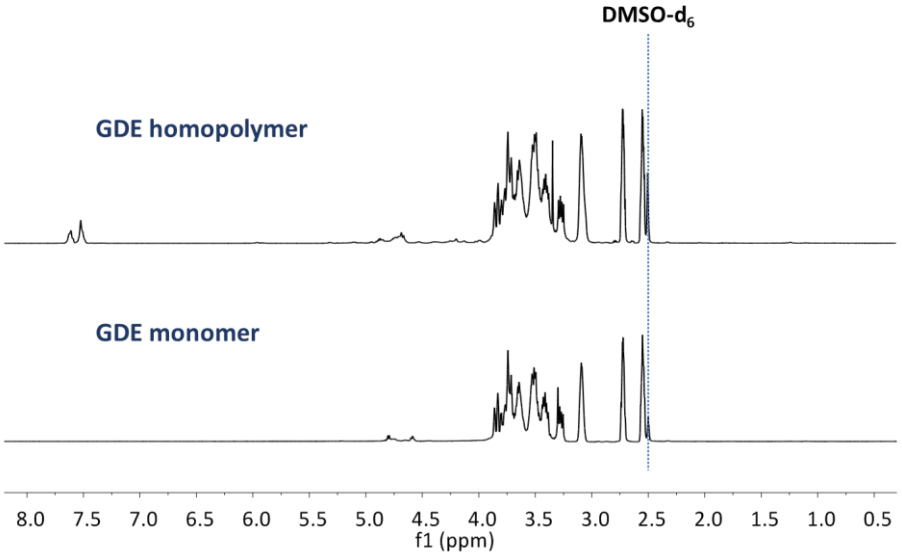

Figure S10. ^{1}H NMR spectra of GDE monomer and GDE homopolymer at t = 6 h.

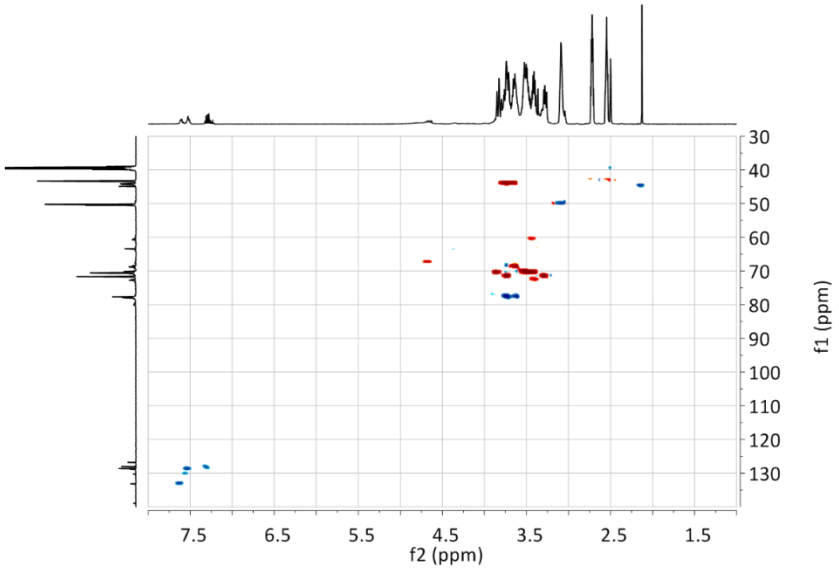

Figure S11. HSQC NMR spectra of GDE homopolymer at t = 0 h. In the spectra, the blue signals correspond to -CH- and -CH_3 signals, while the red ones correspond to -CH_2- signals.

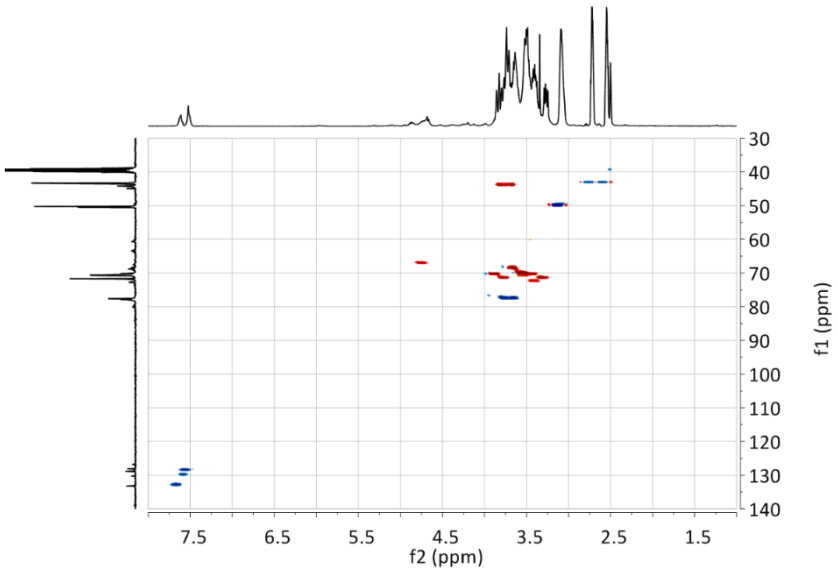

Figure S12. HSQC NMR spectra of GDE homopolymer at t = 6 h. In the spectra, the blue signals correspond to -CH- and -CH_3 signals, while the red ones correspond to -CH_2- signals.

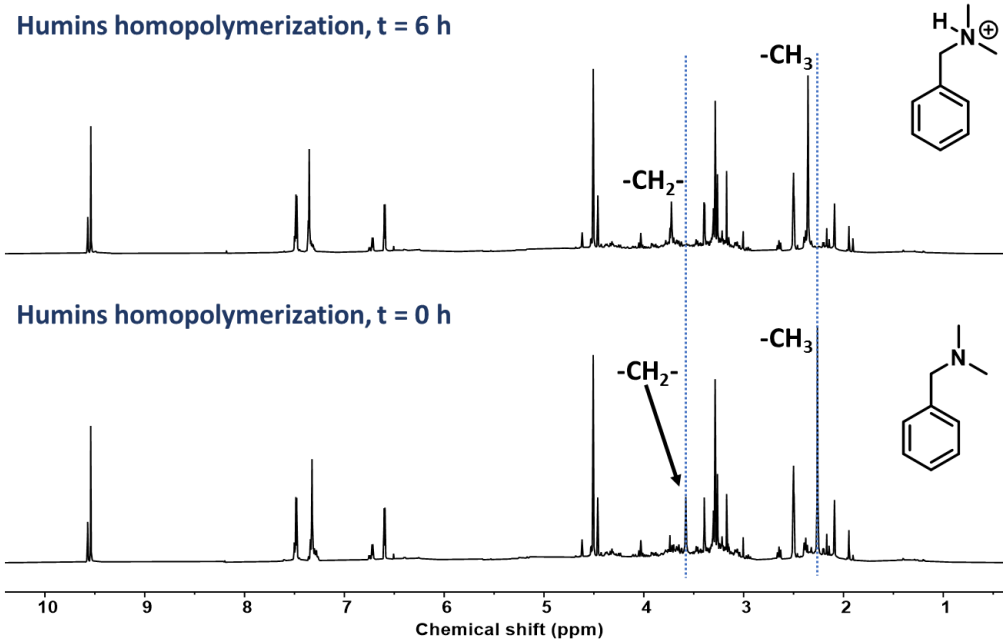

Figure S13. [1]H NMR spectra of humins with BDMA at t = 0 h and the same mixture at t = 6 h.

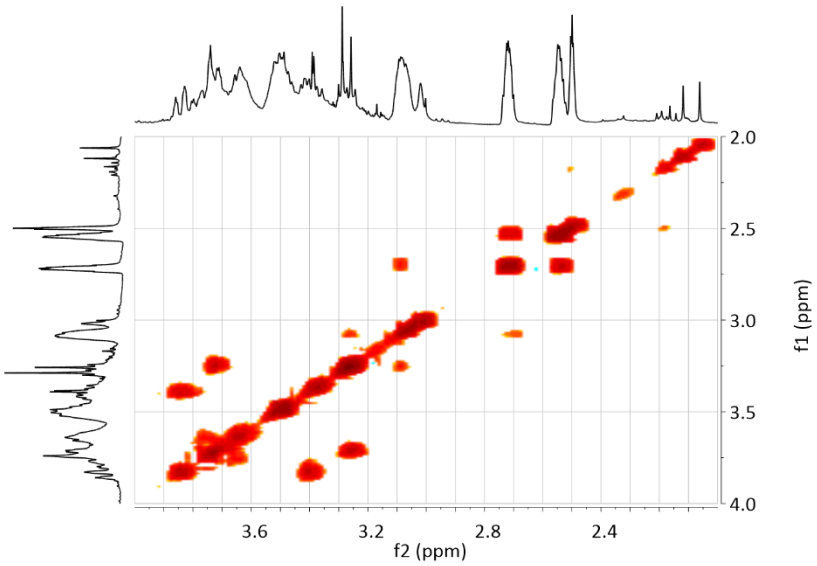

Figure S14. COSY NMR spectra of HG40B5 at t = 0 h.

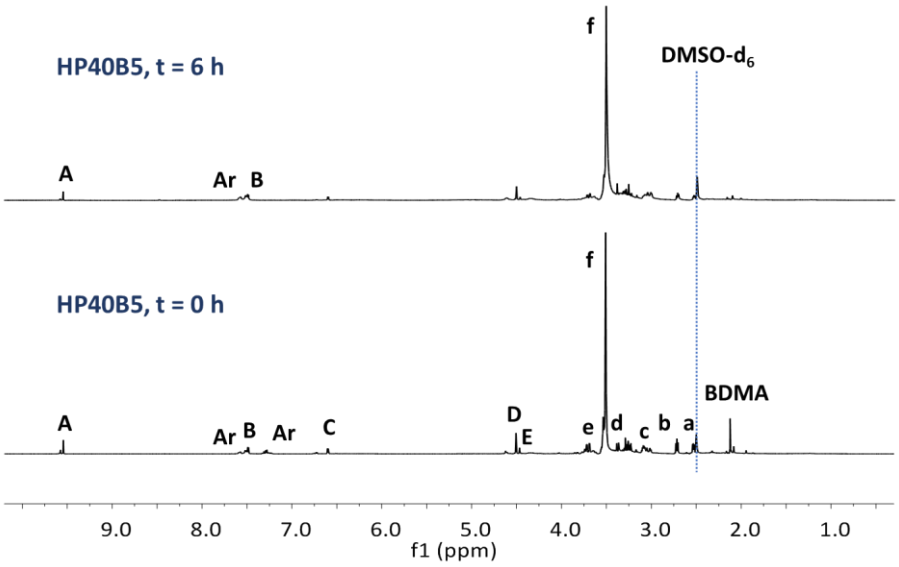

Figure S15. ^{1}H NMR spectra of HP40B5 at t = 0 and at t = 6 h.

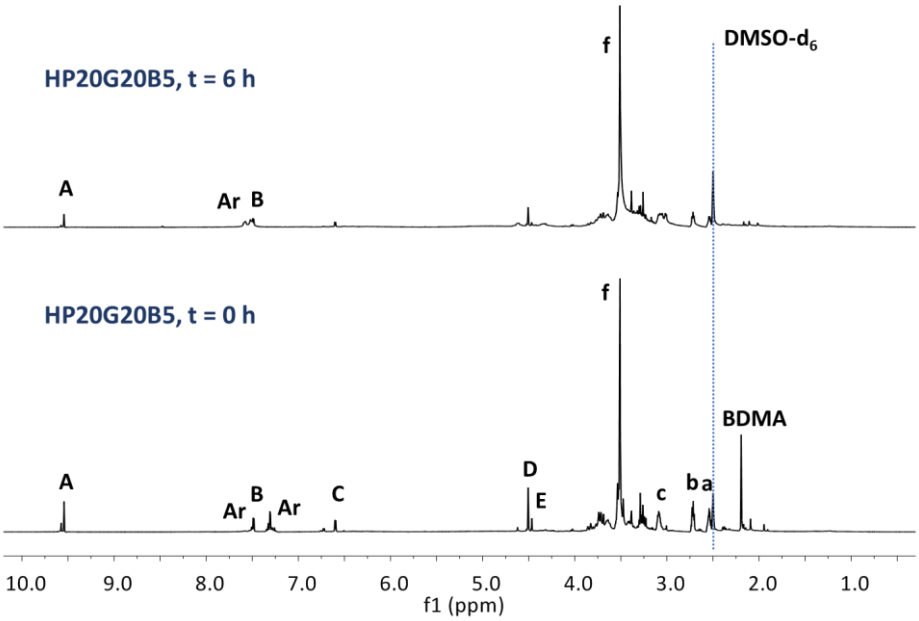

Figure S16. ^{1}H NMR spectra of HP20G20B5 at t = 0 and at t = 6 h.

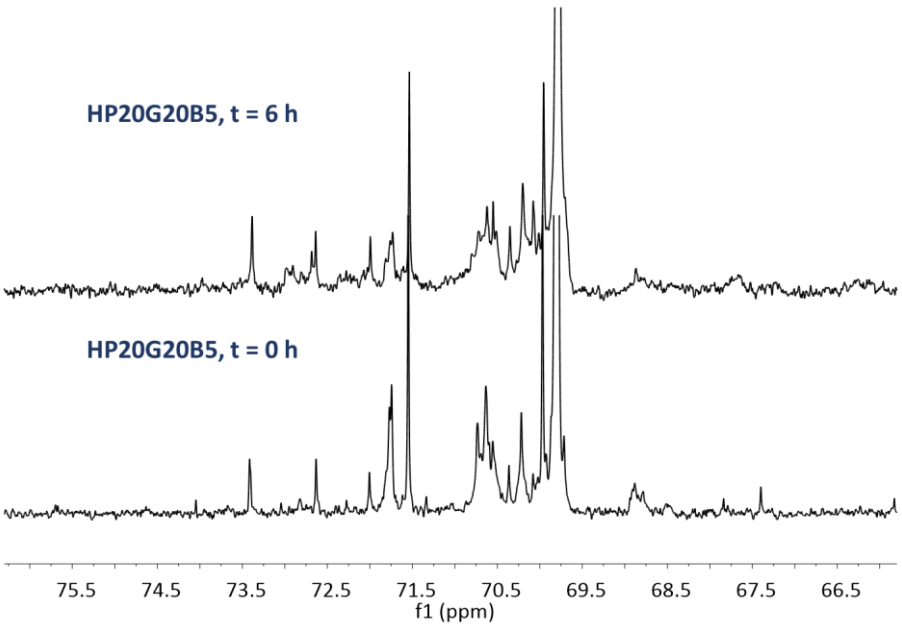

Figure S17. ^{13}C NMR spectra of HP20G20B5 at t = 0 h and t = 6 h.