Supplementary Materials: Synthesis of resins using epoxies and humins as building blocks: A mechanistic study based on in-situ FT-IR and NMR spectroscopies

Xavier Montané¹, Roxana Dinu¹ and Alice Mija^{1,*}

CONTENTS OF THE SUPPORTING INFORMATION

1. Complementary figures for FT-IR spectroscopy investigations

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

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

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

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

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

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

Figure S5. FT-IR spectra of the final HG40B5 copolymers obtained in bulk and in solution.

2. Complementary figures for NMR investigations

Figure S6. Zoom of a) ¹H NMR and b) ¹³C NMR spectra of HG40B5 at t = 0 h and t = 6 h.

Figure S7. ¹H NMR spectra of PGDE, BDMA, humins, HP40B5 at t = 0 h and HP40B5 at t = 6 h.

Figure S8. ¹³C NMR spectra of PGDE, BDMA, humins, HP40B5 at t = 0 h and HP40B5 at t = 6 h.

Figure S9. a) **HSQC NMR spectra of HG40B5 at t = 0 h. b)** zoom of the region between 3.0 – 5.0 ppm in ¹H NMR and 55.0 – 75.0 ppm in ¹³C NMR of the same HSQC NMR spectra. In the spectra, the blue signals correspond to -CH- and -CH₃ signals, while the red ones correspond to -CH₂- signals.

Figure S10. a) HMBC NMR spectra of HG40B5 at t = 0 h. b) Zoom between 2.10 - 2.90 ppm in ¹H NMR and between 171.0 - 179.0 ppm in ¹³C NMR region of the same HMBC NMR spectra.

Figure S11. ¹³C NMR spectra of HP40B5 at t = 0 h and t = 6 h.

Figure S12. ¹H NMR spectra of GDE monomer and GDE homopolymer at t = 6 h.

Figure S13. HSQC NMR spectra of GDE homopolymer at t = 0 h. In the spectra, the blue signals correspond to -CH- and -CH₃ signals, while the red ones correspond to -CH₂- signals.

Figure S14. HSQC NMR spectra of GDE homopolymer at t = 6 h. In the spectra, the blue signals correspond to -CH- and -CH₃ signals, while the red ones correspond to -CH₂- signals.

Figure S15. ¹H NMR spectra of humins with BDMA at t = 0 h and the same mixture at t = 6 h.

Figure S16. COSY NMR spectra of HG40B5 at t = 0 h.

Figure S17. COSY NMR spectra of GDE95B5 (DGE homopolymer) at t = 6 h.

Figure S18. ¹H NMR spectra of HP20G20B5 at t = 0 h and at t = 6 h.

Figure S19. ¹³C NMR spectra of HP20G20B5 at t = 0 h and t = 6 h.

1. Complementary figures for FT-IR spectroscopy investigations



Figure S1. FT-IR spectra of the used initiator (BDMA) and raw materials: GDE, PGDE and 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 -CH3; C-H	
	asymmetric and symmetric bending deformation in -CH2-	
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 S1. Assignment of major bands on FT-IR spectra of humins.

Wavenumber	Assistant	Compound
(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	PGDE, GDE
3000	C-H stretching vibration (-CH-); epoxy group	GDE
3000-2700	C-H stretching vibration (aliphatic)	PGDE, GDE,
		BDMA
2993	C-H stretching vibration (-CH-); epoxy group	PGDE
1490-1410	C-H asymmetric and symmetric bending	PGDE, GDE
	deformation in -CH2-	
1253	C-O-C symmetric stretching vibration of oxirane	GDE
	group; epoxy group	
1251	C-O-C symmetric stretching vibration of oxirane	PGDE
	group; epoxy group	
1092	C-O-C asymmetric stretching vibration; ether linkage	PGDE
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	PGDE
	group; epoxy group	
906	C-O-C asymmetric stretching vibration of oxirane	GDE
	group; epoxy group	
840	C-O-C bending deformation of oxirane group; epoxy	PGDE
	group	
837	C-O-C bending deformation of oxirane group; epoxy	GDE
	group	
758	C-H wagging out-of-plane in epoxy ring (bending)	PGDE
755	C-H wagging out-of-plane in epoxy ring (bending)	GDE
734	C-H out-of-plane bending deformation in the	BDMA
	aromatic ring	
696	C-H out-of-plane bending deformation in the	BDMA
	aromatic ring	

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



Figure S5. FT-IR spectra of the final HG40B5 copolymers obtained in bulk and in solution.

2. Complementary figures for NMR investigations



b) ¹³C NMR



b) ¹³C NMR



HG40B5, t = 6 h 12^{+} HG40B5, t = 0 h 62 60 58 56 54 52f1 (ppm)

Figure S6. Zoom of a) ¹H NMR and b) ¹³C NMR spectra of HG40B5 at t = 0 h and t = 6 h.





Figure S7. ¹³C NMR spectra of PGDE, BDMA, humins, HP40B5 at t = 0 h and HP40B5 at t = 6 h.





Figure S8. ¹³C NMR spectra of PGDE, BDMA, humins, HP40B5 at t = 0 h and HP40B5 at t = 6 h.

b) Zoom of HSQC spectra

Figure S9. a) HSQC NMR spectra of HG40B5 at t = 0 h. b) Zoom of the region between 3.0 - 5.0 ppm in ¹H NMR and 55.0 - 75.0 ppm in ¹³C NMR of the same HSQC NMR spectra. In the spectra, the blue signals correspond to -CH- and -CH₃ signals, while the red ones correspond to -CH₂- signals.

a) HMBC spectra

b) Zoom of HMBC spectra

Figure S10. a) HMBC NMR spectra of HG40B5 at t = 0 h. b) Zoom between 2.10 - 2.90 ppm in ¹H NMR and between 171.0 - 179.0 ppm in ¹³C NMR region of the same HMBC NMR spectra.

Figure S11. ¹³C NMR spectra of HP40B5 at t = 0 h and t = 6 h.

Figure S12. ¹H NMR spectra of GDE monomer and GDE homopolymer at t = 6 h.

Figure S13. HSQC NMR spectra of GDE homopolymer at t = 0 h. In the spectra, the blue signals correspond to -CH- and -CH₃ signals, while the red ones correspond to -CH₂- signals.

Figure S14. HSQC NMR spectra of GDE homopolymer at t = 6 h. In the spectra, the blue signals correspond to -CH- and -CH₃ signals, while the red ones correspond to -CH₂- signals.

Figure S15. ¹H NMR spectra of humins with BDMA at t = 0 h and the same mixture at t = 6 h.

Figure S16. COSY NMR spectra of HG40B5 at t = 0 h.

Figure S17. COSY NMR spectra of GDE95B5 at t = 6 h.

Figure S18. ¹H NMR spectra of HP20G20B5 at t = 0 h and at t = 6 h.

Figure S19. ¹³C NMR spectra of HP20G20B5 at t = 0 h and t = 6 h.