Some Key Factors Influencing the Flame Retardancy of EDA-DOPO Containing Flexible Polyurethane Foams

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All 1H, 13C and 31P NMR spectra were recorded on a Bruker Avance III 400 NMR spectrometer (Bruker Biospin AG, Fällanden, Switzerland) at 400.2, 100.6, and 162.0 MHz, respectively. The 1D NMR spectra, as well as the 1H-13C HSQC, 1H-13C HMBC, 1H-13C HSQC-TOCSY, 1H-H DQF-COSY, and 1H-31P HMBC 2D correlation NMR experiments used for the complete assignment of resonances were performed at 298 K using the Bruker standard pulse programs and parameter sets on a 5 mm CryoProbe™ Prodigy probe equipped with z-gradient applying 90° pulse lengths of 11.4 µs (1H), 10.0 µs (13C) and 12.0 µs (31P). 1H and 13C chemical shifts (δ) in ppm are calibrated to residual solvent peaks (DMSO-d6: δ = 2.49 and 39.5 ppm), the 31P chemical shifts were referenced to an external sample with neat H3PO4 at 0.0 ppm. Since all reported compounds consist of two inseparable diastereomers the coupling patterns of the 1H NMR spectra remain complex and no reliable J values could be extracted. Wherever possible, the 1H, 31P coupling constants are reported in Hz. For 13C NMR data multiplicities = quaternary carbon, d = CH, t = CH2, and q = CH3 are shown and 31P, 13C coupling constants are reported in Hz. Weak correlations observed in the 2D NMR experiments are assigned as "w". For EG-DOPO and ETA-DOPO nearly 1:1 mixture of diastereomers were found disabling the discrimination of the generally doubled set of 13C signals of the individual species by the heights of carbon resonances as it was possible for EDA-DOPO.

EG-DOPO (2 isomers, ca. 1:1)

1H NMR (400.2 MHz, DMSO-d6) δ (ppm): 8.19 (m, J(H,P) = 6.2, 2H, H-5); 8.14 (m, 2H, H-8); 7.71 (m, J(H,P) = 14.4, 2H, H-2); 7.53 (m, J(H,P) = 3.6, 2H, H-3); 7.41 (m, 2H, H-10); 7.30 (m, 2H, H-9); 7.18 (m, 2H, H-11); 4.18 (m, 4H, H-13).

13C NMR (100.6 MHz, DMSO-d6) δ (ppm): 148.5 (sd, J(C,P) = 7.8, C-12); 136.2 (sd, J(C,P) = 7, C-6); 134.0 (dd, J(C,P) = 2.5, C-4); 130.8 (d, C-10); 129.7 (dd, J(C,P) = 9.4, C-2); 128.6 (dd, J(C,P) = 15.2, C-3); 125.8 (d, C-8); 125.0 (d, C-9); 124.6 (dd, J(C,P) = 11.8, C-5); 121.8 (sd, J(C,P) = 11.8, C-7); 121.3 (sd, J(C,P) = 179.4, C-1); 119.8 (dd, J(C,P) = 6.6, C-11); 65.2 (td, J(C,P) = 5.9/1.9, C-13).

31P NMR (162.0 MHz, DMSO-d6) δ (ppm): 9.9

1H-13C HMBC: H-2 → C-(1w, 4, 6); H-3 → C-(1, 4w, 5); H-4 → C-(2, 5w, 6); H-5 → C-(1, 3, 7); H-8 → C-(6, 10, 12); H-9 → C-(7, 11); H-10 → C-(8, 11w, 12); H-11 → C-(7, 9, 12); H-13 → C-(13); H-2 → C-(2, 4, 5); H-3 → C-(1, 3); H-4 → C-(2); H-5 → C-(1, 2, 6, 9); H-6 → C-(5, 7, 8, 9); H-8 → C-(6); H-9 → C-(5w, 6).

1H-H DQF-COSY: H-2 → H-(3); H-3 → H-(2, 4); H-4 → H-(3, 5); H-5 → H-(4); H-8 → H-(9); H-9 → H-(8, 10); H-10 → H-(9, 11); H-11 → H-(10); H-13 → H-(14).

1H-31P HMBC: H-(2, 3, 5, 13) → P

EDA-DOPO (2 isomers, ca. 1.2:0.8)

Major isomer (60%)

1H NMR (400.2 MHz, DMSO-d6) δ (ppm): 8.14 (m, J(H,P) = 3.1, 2H, H-5); 8.10 (m, 2H, H-8); 7.77 (m, J(H,P) = 22.1, 2H, H-2); 7.70 (m, 2H, H-4); 7.50 (m, J(H,P) = 3, 2H, H-3); 7.39 (m, 2H, H-10); 7.27 (m, 2H, H-9); 7.15 (m, 2H, H-11); 5.75 (m, J(H,P) = 11.8, 2H, NH); 2.85 (m, 4H, H-13).

13C NMR (100.6 MHz, DMSO-d6) δ (ppm): 149.4 (sd, J(C,P) = 7.2, C-12); 135.9 (sd, J(C,P) = 6.7, C-6); 132.7 (d, C-4); 130.4 (d, C-10); 129.4 (dd, J(C,P) = 9.6, C-2); 128.3 (dd, J(C,P) = 14.3, C-3); 125.4 (dd, J(C,P) = 0.6, C-8); 125.2 (sd, J(C,P) = 161.9, C-1); 124.2 (d, C-9); 124.1 (dd, J(C,P) = 10.7, C-5); 121.9 (sd, J(C,P) = 11.5, C-7); 120.0 (dd, J(C,P) = 5.9, C-11); 41.7 (td, J(C,P) = 5.6, C-13).

31P NMR (162.0 MHz, DMSO-d6) δ (ppm): 15.2

1H-13C HMBC: H-2 → C-(1w, 4, 6); H-3 → C-(1, 2w, 5); H-4 → C-(2, 5w, 6); H-5 → C-(1, 3, 7); H-8 → C-(6, 10, 12); H-9 → C-(7, 11); H-10 → C-(8, 11w, 12); H-11 → C-(7, 9, 12); H-13 → C-(13); H-2 → C-(2, 4, 5); H-3 → C-(1, 3); H-4 → C-(2); H-5 → C-(1, 2, 6, 9); H-6 → C-(5, 7, 8, 9); H-8 → C-(6); H-9 → C-(5w, 6).

1H-H DQF-COSY: H-2 → H-(3); H-3 → H-(2, 4); H-4 → H-(3, 5); H-5 → H-(4); H-8 → H-(9); H-9 → H-(8, 10); H-10 → H-(9, 11); H-11 → H-(10); H-13 → H-(14).

1H-31P HMBC: H-(2, 3, 5, 13) → P
**Supplementary information**

**Minor Isomer (40%)**

1H NMR (400.2 MHz, DMSO-d<sub>6</sub>) δ (ppm): 8.14 (m, J(H,P) = 3.1, 2H, H-5); 8.10 (m, 2H, H-8); 7.77 (m, J(H,P) = 22.1, 2H, H-2); 7.70 (m, 2H, H-4); 7.50 (m, J(H,P) = 3, 2H, H-3); 7.39 (m, 2H, H-10); 7.27 (m, 2H, H-9); 7.15 (m, 2H, H-11); 5.75 (m, J(H,P) = 11.8, 2H, NH); 2.85 (m, 4H, H-13).

13C NMR (100.6 MHz, DMSO-d<sub>6</sub>) δ (ppm): 149.3 (sd, J(C,P) = 7.1, C-12); 136.0 (sd, J(C,P) = 6.8, C-6); 132.7 (d, C-4); 130.3 (d, C-10); 129.4 (dd, J(C,P) = 9.7, C-2); 128.3 (dd, J(C,P) = 14.3, C-3); 125.4 (dd, J(C,P) = 0.7, C-8); 125.2 (sd, J(C,P) = 161.9, C-1); 124.2 (d, C-9); 124.1 (dd, J(C,P) = 10.8, C-5); 121.9 (sd, J(C,P) = 11.5, C-7); 120.0 (dd, J(C,P) = 5.6, C-11); 41.7 (td, J(C,P) = 5.6, C-13).

31P NMR (162.0 MHz, DMSO-d<sub>6</sub>) δ (ppm): 15.3

**1H-13C HMBC:** H-2 → C-(1w, 4, 6); H-3 → C-(1, 2w, 5); H-4 → C-(2, 3w, 6); H-5 → C-(1, 3, 7); H-8 → C-(6, 10, 12); H-9 → C-(7, 8w, 11); H-10 → C-(7, 9, 12); H-11 → C-(9, 11, 12); H-13 → C-(13); NH → C-(13w).

**1H-1H DQF-COSY:** H-2 → H-(3); H-3 → H-(2, 4); H-4 → H-(3, 5); H-5 → H-(4); H-8 → H-(9); H-9 → H-(8, 10); H-10 → H-(9, 11); H-11 → H-(10); H-13 → H-(14); NH → H-(13).

**1H-31P HMBC:** H-(2, 3, 5, 13, NH) → P

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**ETA-DOPO (2 isomers, ca. 1:1)**

1H NMR (400.2 MHz, DMSO-d<sub>6</sub>) δ (ppm): 8.24 (m, J(H,P) = 6.2, 1H, H-18); 8.18 (m, 1H, H-21); 8.14 (m, 1H, H-5); 8.12 (m, 1H, H-8); 7.89 (m, J(H,P) = 14.6, 1H, H-15); 7.83 (m, 1H, H-17); 7.71 (m, 1H, H-4); 7.65 (m, J(H,P) = 14, 1H, H-2); 7.61 (m, J(H,P) = 3.6, 1H, H-16); 7.45 (m, 1H, H-23); 7.44 (m, 1H, H-3); 7.40 (m, 1H, H-10); 7.32 (m, 1H, H-22); 7.28 (m, 1H, H-9); 7.27 (m, 1H, H-24); 7.12 (m, 1H, H-11); 5.83 (m, J(H,P) = 11.8, 1H, NH); 4.02 (m, 2H, H-26); 3.00 (m, 2H, H-13).

13C NMR (100.6 MHz, DMSO-d<sub>6</sub>) δ (ppm): 149.3 (sd, J(C,P) = 7.1, C-12); 149.2 (sd, J(C,P) = 7.9, C-25); 136.2 (sd, J(C,P) = 7.1, C-19); 135.9 (sd, J(C,P) = 7, C-6); 134.0 (dd, J(C,P) = 2.4, C-17); 132.7 (d, C-4); 130.9 (d, C-23); 130.4 (d, C-10); 129.9 (dd, J(C,P) = 9.3, C-15); 129.4 (dd, J(C,P) = 9.7, C-2); 128.7 (dd, J(C,P) = 15.1, C-16); 128.3 (dd, J(C,P) = 14.3, C-3); 125.9 (d, C-21); 125.4 (dd, J(C,P) = 0.6, C-8); 125.3 (sd, J(C,P) = 162.9, C-1); 125.1 (d, C-22); 124.6 (dd, J(C,P) = 11.7, C-18); 124.3 (d, C-9); 124.1 (dd, J(C,P) = 10.7, C-5); 122.0 (sd, J(C,P) = 11.8, C-20); 121.9 (sd, J(C,P) = 11.6, C-7); 121.5 (sd, J(C,P) = 178.9, C-14); 120.1 (dd, J(C,P) = 5.9, C-11); 119.9 (dd, J(C,P) = 6.5, C-24); 66.1 (t, C-26); 40.4 (td, J(C,P) = 7.3, C-13).

31P NMR (162.0 MHz, DMSO-d<sub>6</sub>) δ (ppm): 14.6 (P<sub>a</sub>); 9.8 (P<sub>b</sub>).

**1H-13C HMBC:** H-2 → C-(4, 6); H-3 → C-(1, 5); H-4 → C-(2, 6); H-5 → C-(1, 3, 7); H-8 → C-(6, 10, 12); H-9 → C-(7, 11); H-10 → C-(8, 12); H-11 → C-(7, 9, 12); H-13 → C-(26); NH → H-(13); H-15 → C-(17, 19); H-16 → C-(14, 18); H-17 → C-(15, 19); H-18 → C-(6, 14, 20); H-21 → C-(19, 23, 25); H-22 → C-(20, 24); H-23 → C-(21, 25); H-24 → C-(20, 22, 25); H-26 → C-(13).

**1H-1H DQF-COSY:** H-2 → H-(3); H-3 → H-(2, 4); H-4 → H-(3, 5); H-5 → H-(4); H-8 → H-(9); H-9 → H-(8, 10); H-10 → H-(9, 11); H-11 → H-(10); H-13 → H-(14); NH → H-(13).

**1H-31P HMBC:** H-(2, 3, 5, 13, NH) → P<sub>a</sub>; H-(15, 16, 18, 26) → P<sub>b</sub>.
**Figure S1a.** $^1$H, $^{13}$C and $^{31}$P NMR spectra of EG-DOPO (DMSO-d$_6$).

**Figure S1b.** Regions of interest of $^1$H-$^{13}$C HSQC (A, B), $^1$H-$^{13}$C HMBC (C), and $^1$H-$^1$H DQF-COSY (D) NMR spectra of EG-DOPO (DMSO-d$_6$).
Figure S1c. $^1$H, $^{13}$C and $^{31}$P NMR spectra of ETA-DOPO (DMSO-d$_6$)

Figure S1d. Regions of interest of $^1$H-$^{13}$C HSQC (A, B), $^1$H-$^{13}$C HMBC (C) and $^1$H-$^1$H DQF-COSY (D) NMR spectra of ETA-DOPO (DMSO-d$_6$).
**Figure S1e.** $^1$H, $^{13}$C, and $^{31}$P NMR spectra of EDA-DOPO (DMSO-d$_6$).

**Figure S1f.** Regions of interest of $^1$H-$^{13}$C HSQC (A, B), $^1$H-$^{13}$C HMBC (C), and $^1$H-$^1$H DQF-COSY (D) NMR spectra of EDA-DOPO (DMSO-d$_6$).
**Figure S2.** TGA data of bridged DOPO compounds (N₂ atmosphere).

**Figure S3.** TGA data of PU foams containing 5% bridged DOPO compounds (N₂ atmosphere).