Electronic Supplementary Material (ESI) for Polymer Chemistry.
This journal is © The Royal Society of Chemistry 2024

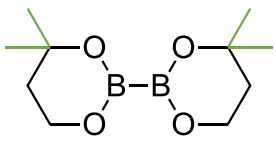
Supporting Information

Boron-Boron Bonds: Boldly Breaking Boundaries towards Amine- and Peroxide-Free 2K Radical Polymerization

Florian Pieringer[a], Konstantin Knaipp[b], Robert Liska[a], Norbert Moszner[c], Yohann Catel[c], Georg Gescheidt[b], Patrick Knaack[a]*

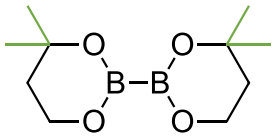
Materials

B6-1 (5,5,5',5'-Tetramethyl-2,2'-bi-1,3,2-dioxaborinan) (98%, BLD Pharm), B6-3 (4,4,4',4',6,6,6',6'-Octamethyl-2,2'-bi(1,3,2-dioxaborinane)) (97%, BLD Pharm), B5-1 (4,4,4',4',5,5,5',5'-Octamethyl-2,2'-bi-1,3,2-dioxaborolan) (99%, Merck), B5-2 (4,8-Dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,6,2-dioxazaborocane) (95%, abcr), B5-3 (2-(Dimethylphenylsilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan) (95%, Merck), D3MA (Decandioldimethacrylate) (Ivoclar AG), UDMA (Urethanedimethacrylate) (Ivoclar AG), BisGMA (Bisphenol-A-glycidyl-dimethacrylate) (Ivoclar AG), $Cu(acac)_2$ (99.9%, Merck), $Cu(tfacac)_2$ (99%, abcr), $Cu(hfacac)_2$ (99%, Merck), $Cu(ac)_2$ (98%, Merck), Cu(ac) (98%, abcr), Tetrakis(dimethylamino)diboron (98%, BLD Pharm), 3-methylbutane-1,3-diol (97%, Merck) were used as received.

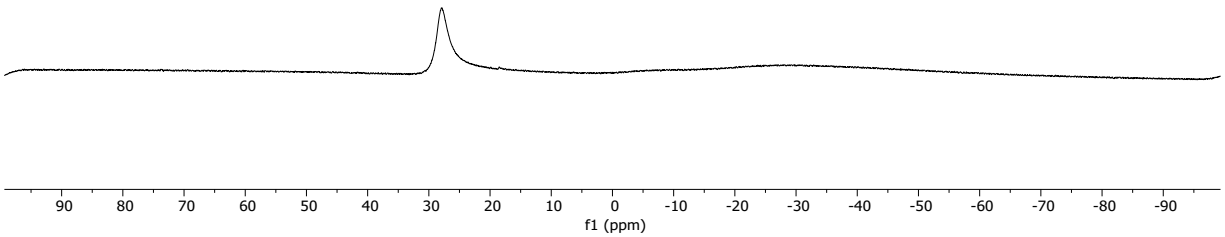


B6-2

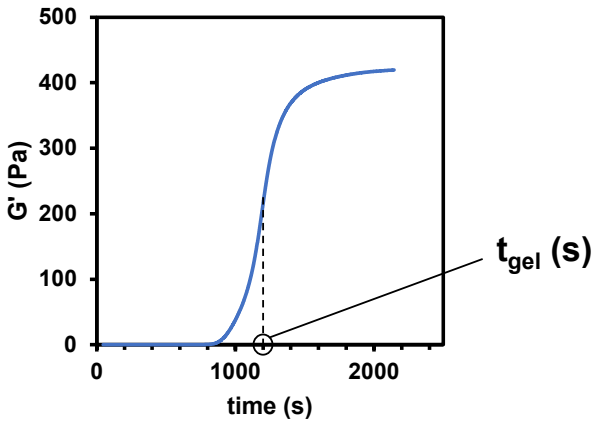
SI Figure 1: ^{1}H NMR of B6-2



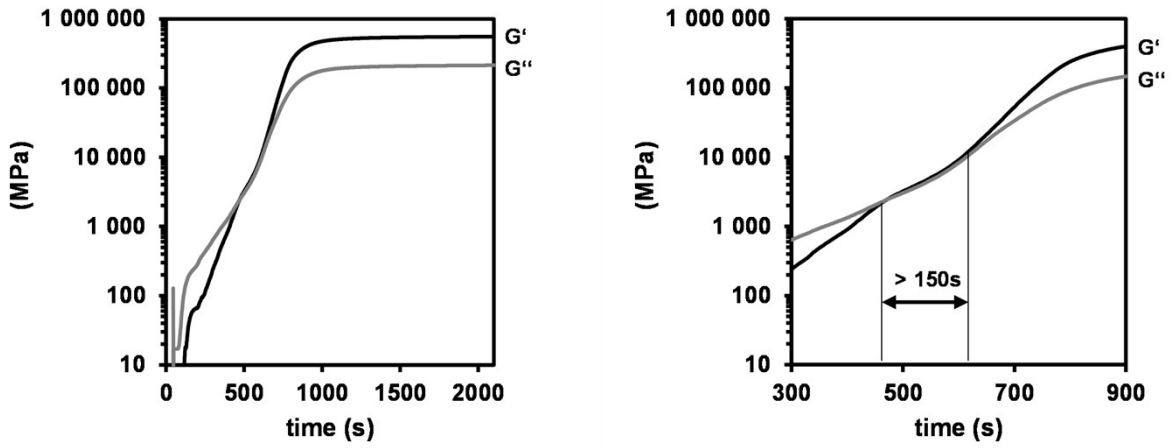
B6-2



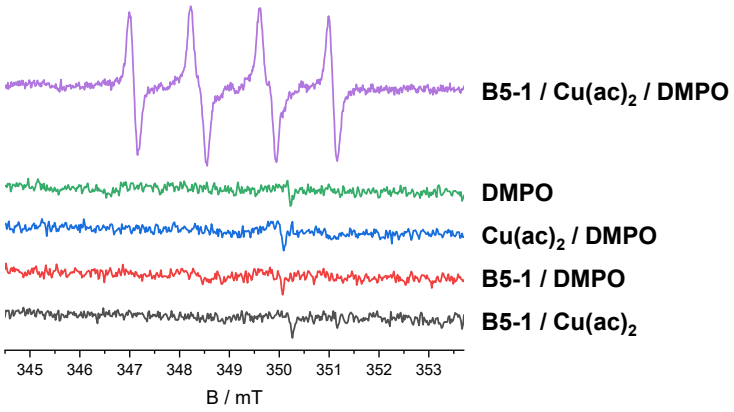
SI Figure 2: ^{11}B NMR of B6-2



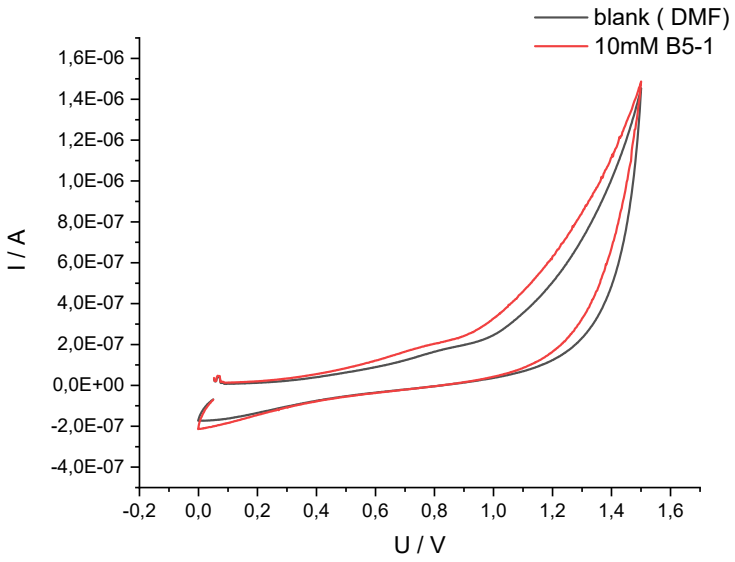
SI Figure 3: Schematic explanation of t_{gel} as the time of maximum increase in G'.



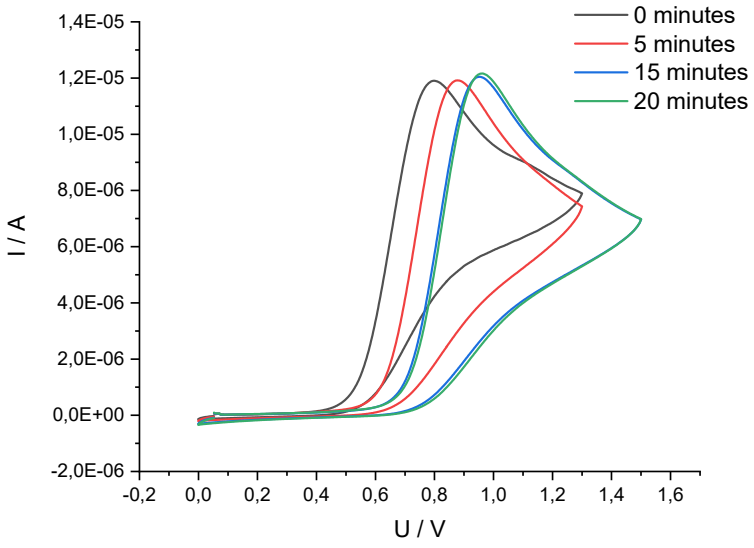
SI Figure 4: Rheology/IR measurement, showing the parallel section of G’ and G’’, making it not viable to use the intersection of those parameters for evaluation of t_{gel}.



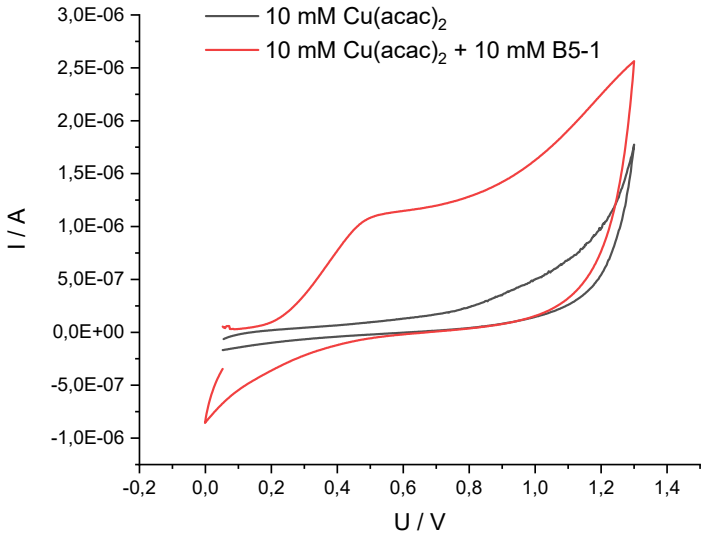
SI Figure 5: Blank experiment with ESR-ST



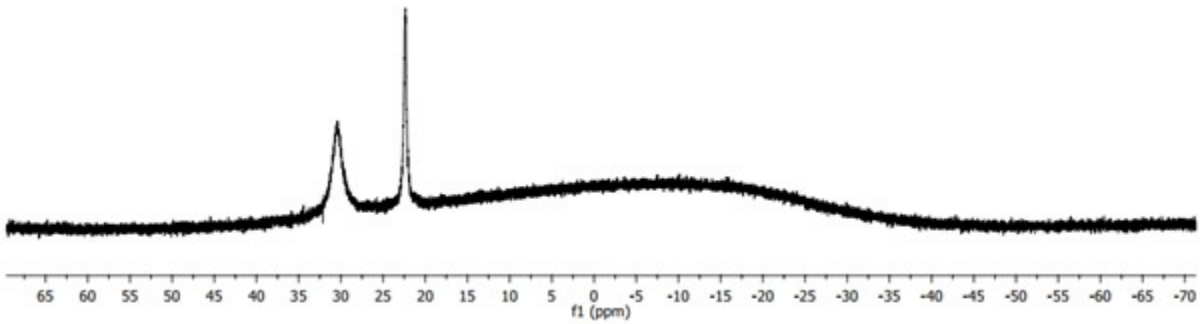
SI Figure 6: Cyclic voltammetry measurement of a blank sample and a 10 mM solution of B5-1 in dimethylformamide.



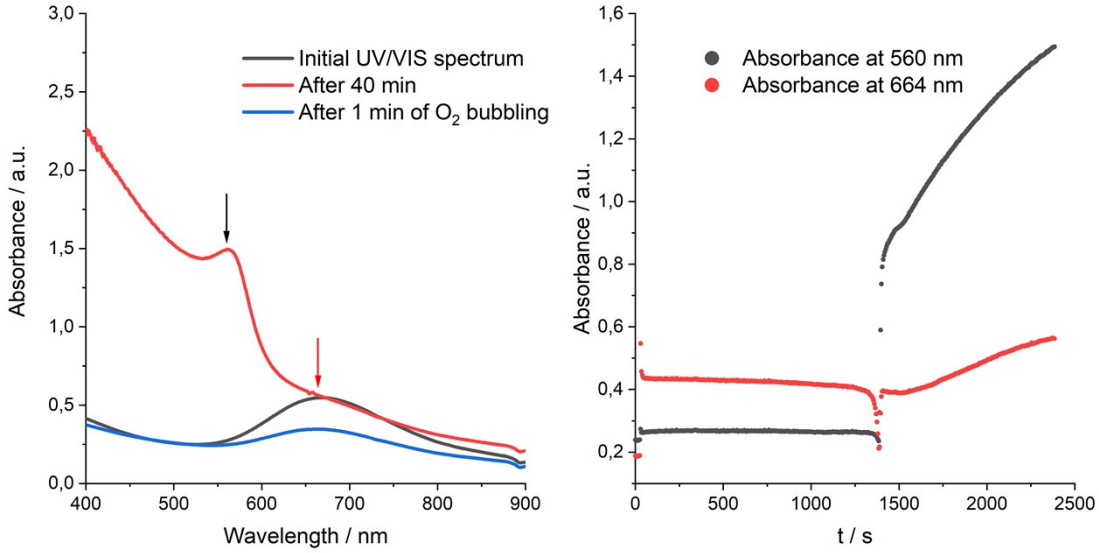
SI Figure 7: Cyclic voltammetry measurements of a 10 mM solution of Na(acac) after addition of 10 mM B5-1. Additional cyclovoltammograms are recorded after 5, 15 and 20 minutes respectively.



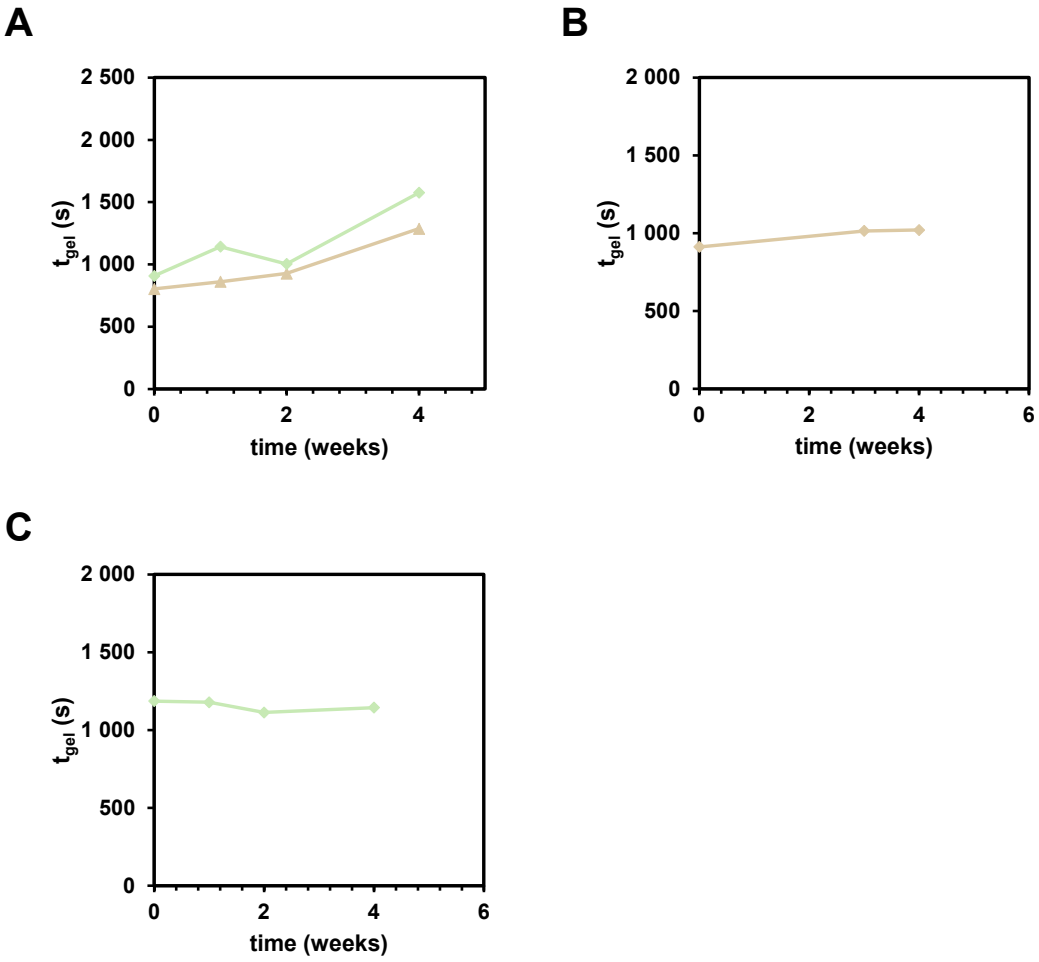
SI Figure 8: Cyclic voltammetry measurements of a 10 mM solution of $Cu(acac)_2$ before and after addition of 1 equivalent B5-1.



SI Figure 9: ^{11}B NMR of a solution of $Cu(ac)_2$ (1.14 mM) and B5-1 (20 mM) in deuterated acetonitrile. The spectrum was recorded one hour after the degassed stock solutions were combined.

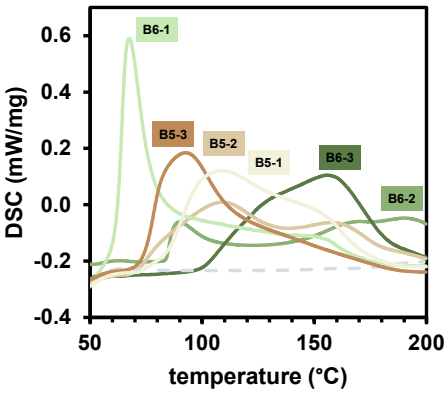


SI Figure 10: On the left, UV/Vis spectroscopy of a solution containing B5-1 (20 mM), $Cu(ac)_2$ (1.14 mM) and methylmethacrylate (100 mM) in dry acetonitrile. Spectra shown are recorded immediately after combining the degassed stock solutions, after 40 minutes and after bubbling the solution with O_2 for one minute. Kinetic traces are shown on the right.

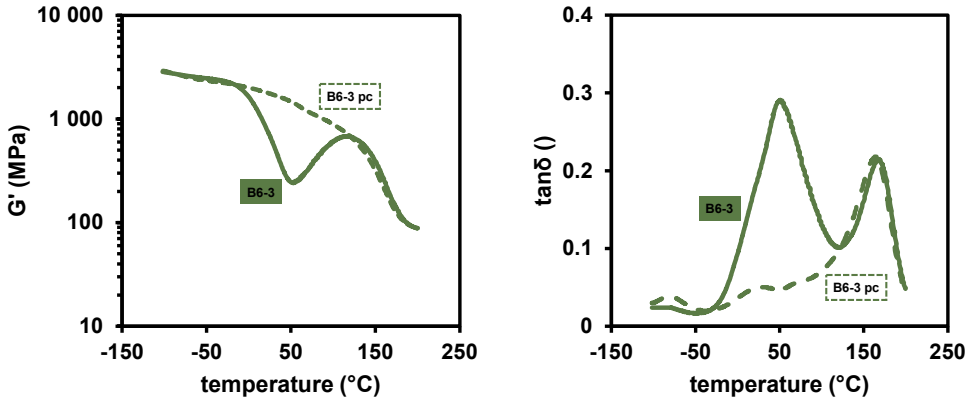


SI Figure 11: A: Long-time reactivity displayed as progression of t_{gel} over time. B6-1 (green) and B5-2 (brown) were investigated in Mix-3. **B:** Long-time reactivity displayed as progression of t_{gel} over time. B5-2 (brown) was investigated in D3MA/BisGMA (1:3 (w%)). **C:** Long-time reactivity displayed as progression of t_{gel} over time. B6-1 (green) was investigated in pure D3MA.

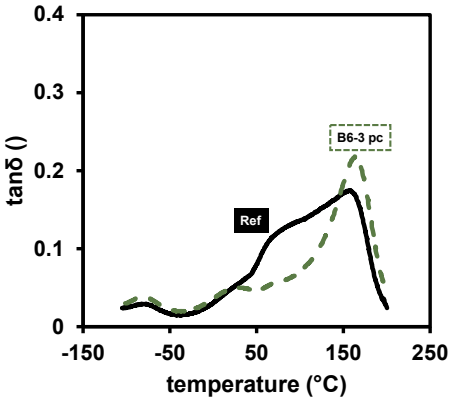
SI Figure 12: Picture of cured specimen, showing no discoloration after weeks of storage. For better visibility one picture was taken in front of a black background and one in front of a white background.



SI Figure 13: DSC measurements to confirm thermal polymerization of Mix-3 with diborane compounds. To evaluate the thermal polymerization of the formulations under investigation DSC experiments were conducted using a Netzsch Jupiter STA 449 F1 thermal analysis tool with an autosampler. The experiments involved a ramp from 25 to 200 °C under N_2 atmosphere (10 K min^{-1}), which was performed twice to gather a baseline. All samples were precisely weighed into aluminum DSC pans (10 ± 2 mg) and subjected to a constant gas flow rate (40 mL min^{-1}). The DSC signal was recorded.



SI Figure 14: Left: Progression of G' during DMTA measurement without (solid line) and with (dashed line) post-curing for 24h at 100 °C. Right: Progression of tanδ during DMTA measurement without (solid line) and with (dashed line) post-curing for 24h at 100 °C. Post-curing possible, reaching T_g > 150°C.



SI Figure 15: Very narrow T_g of the B6-3/$Cu(acac)_2$ cured formulation after post-curing compared to commercial FRP (CHP/$Cu(acac)_2$/Thiourea)[50] polymerized Mix-3, showing a homogeneous network structure.