Electronic Supplementary Information

Efficient synthesis of 2-methylene-4-phenyl-1,3-dioxolane, a cyclic ketene acetal for controlling the NMP of methyl methacrylate and conferring tunable degradability

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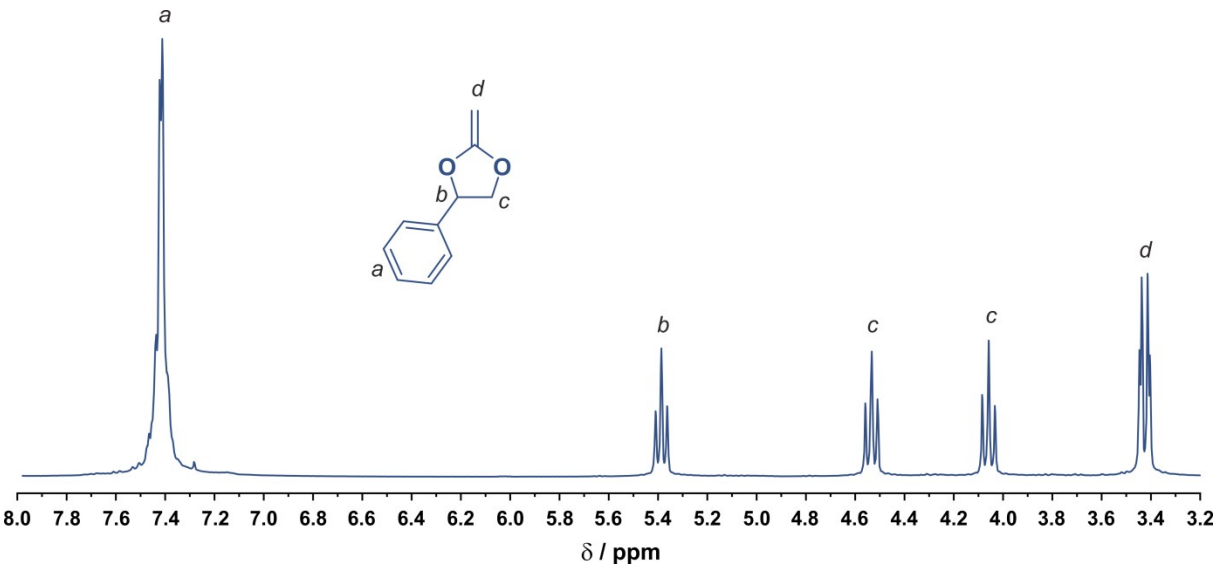

Figure S1. Representative ^{1}H NMR spectrum in $CDCl_3$ in the 3.2–8.0 ppm region of MPDL.

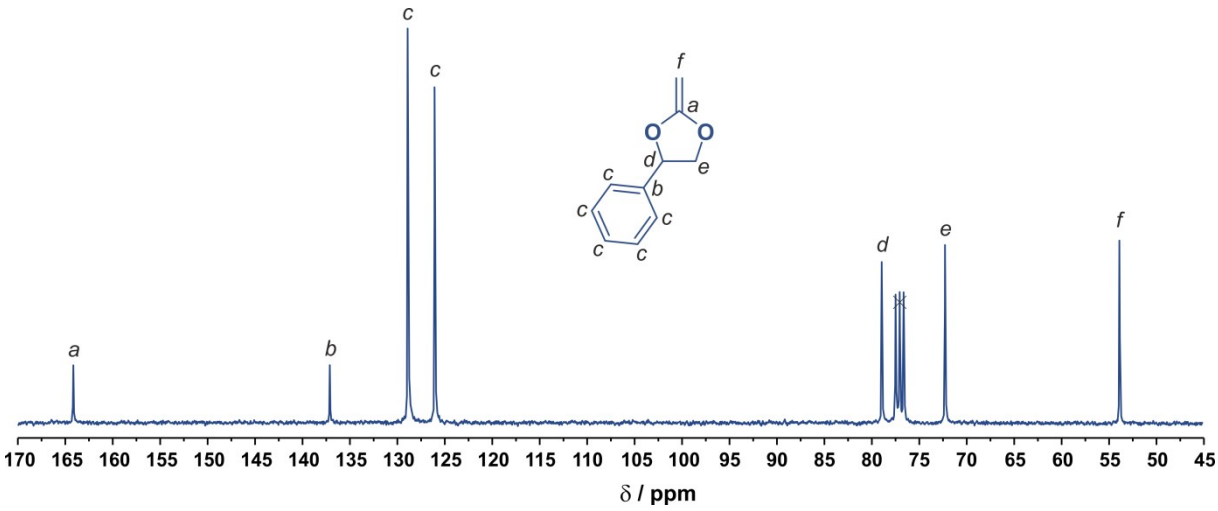

Figure S2. Representative ^{13}C NMR spectrum in $CDCl_3$ in the 45–170 ppm region of MPDL.

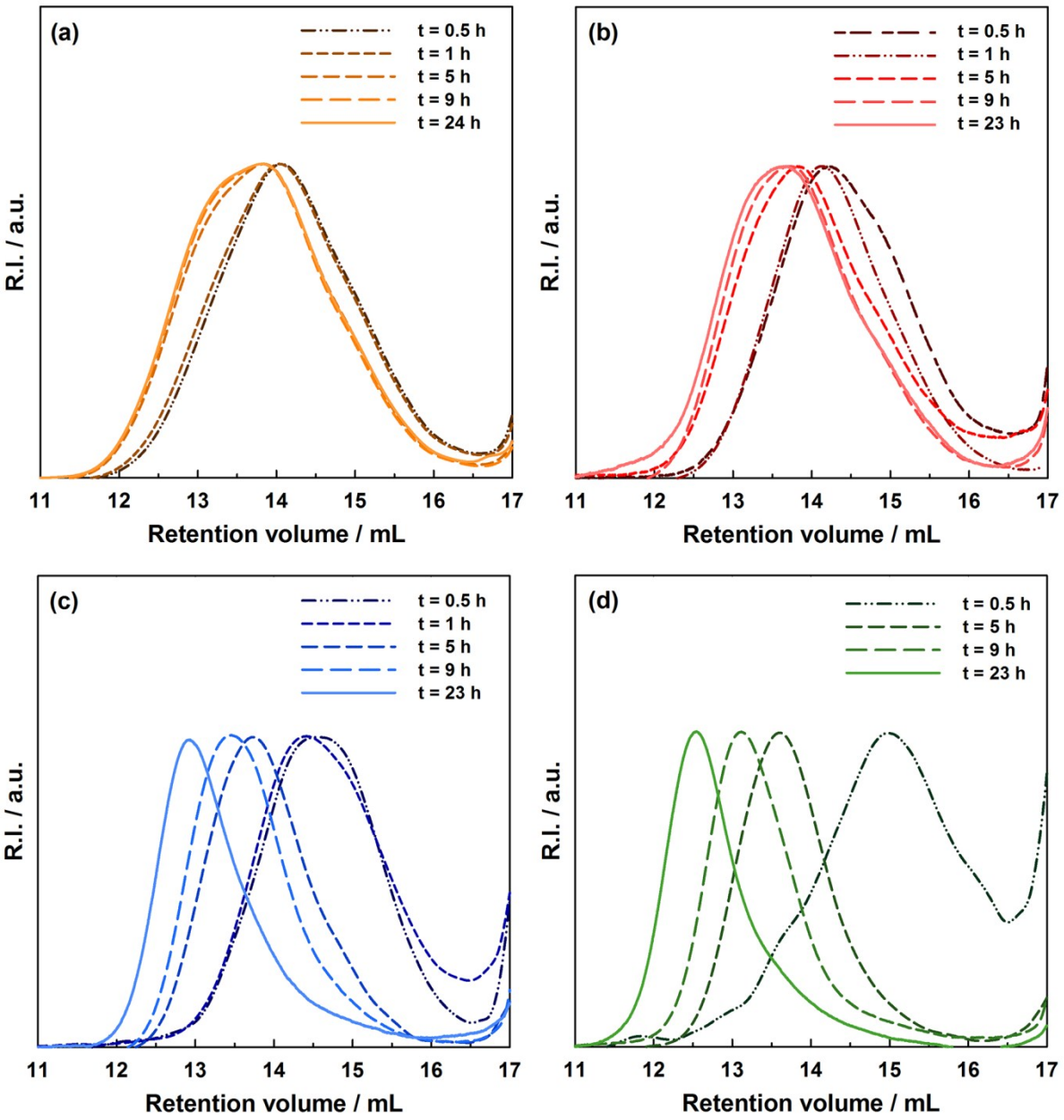

Figure S3. SEC traces taken at different time intervals during the NMP of MMA and MPDL in toluene initiated by the BlocBuilder alkoxyamine at 90 °C, as a function of the initial amount of MPDL: (a) expt. **1** ($f_{MPDL,0}$ = 0.1); (b) expt. **2** ($f_{MPDL,0}$ = 0.2); (c) expt. **3** ($f_{MPDL,0}$ = 0.4); (d) expt. **4** ($f_{MPDL,0}$ = 0.7).

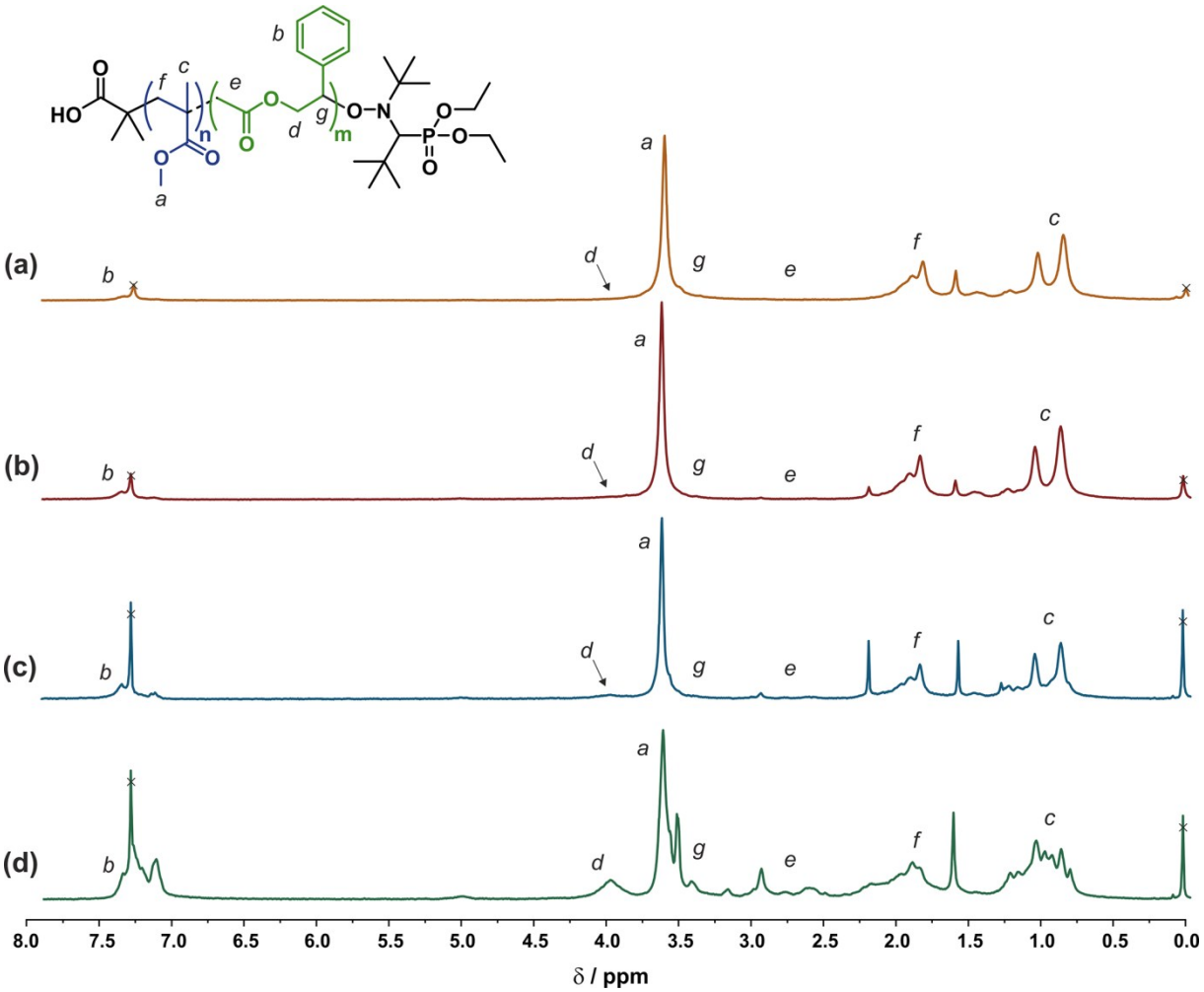

Figure S4. ^{1}H NMR spectra in $CDCl_3$ of the purified copolymers resulting from the NMP of MMA and MPDL in toluene initiated by the BlocBuilder alkoxyamine at 90 °C, as a function of the initial amount of MPDL: (a) expt. **1'** ($f_{MPDL,0} = 0.1$); (b) expt. **2'** ($f_{MPDL,0} = 0.2$); (c) expt. **3'** ($f_{MPDL,0} = 0.4$); (d) expt. **4'** ($f_{MPDL,0} = 0.7$).

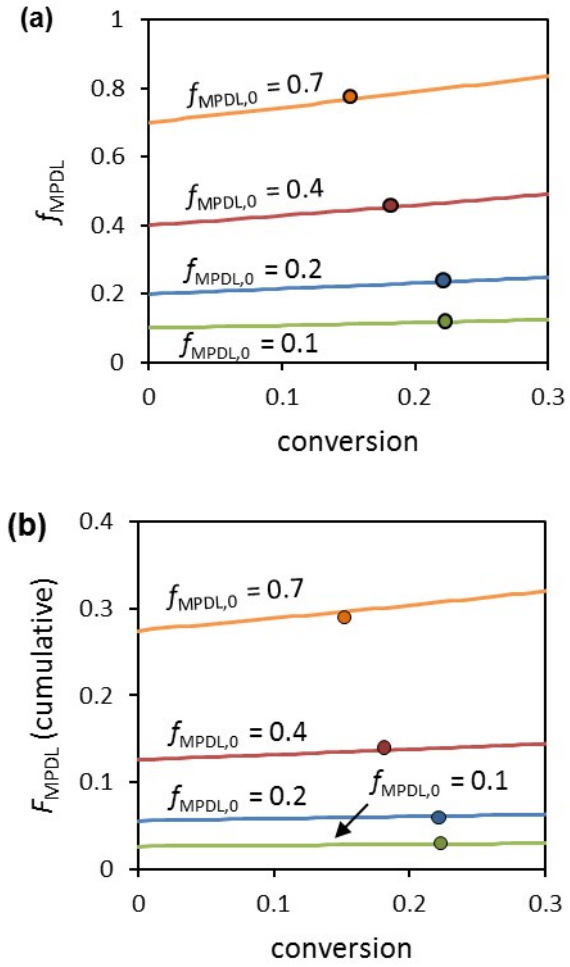

Figure S5. Comparison of modeled and experimental data for (a) the monomer feed ratio and (b) the cumulative copolymer composition as a function of conversion. Modeled data were obtained by nonlinear least squared fitting of the integrated copolymer composition equation to the experimental data, yielding reactivity ratios of $r_{MPDL} = 0.01$, $r_{MMA} = 4.0$.

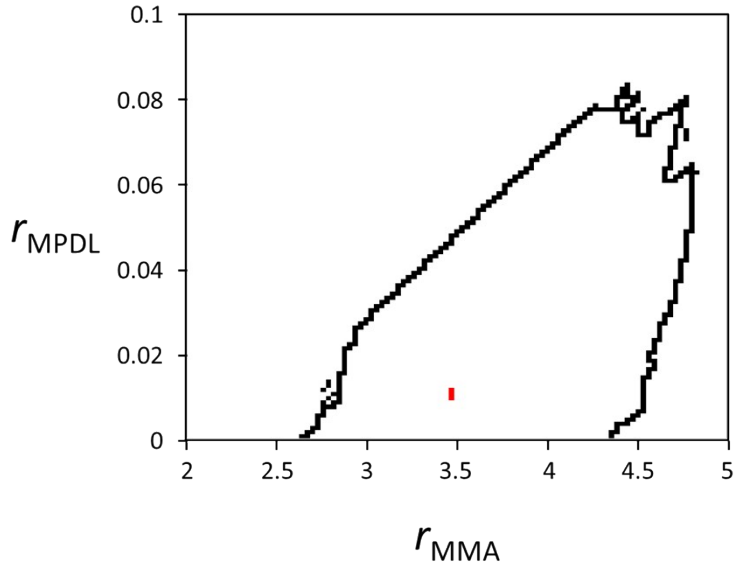

Figure S6. 95% joint confidence region for reactivity ratios of MPDL and MMA, calculated by the 'visualisation of the sum of least squares space' method of van den Brink et al.[1] The red point represents the best estimate of $r_{MPDL} = 0.01$, $r_{MMA} = 4.0$.

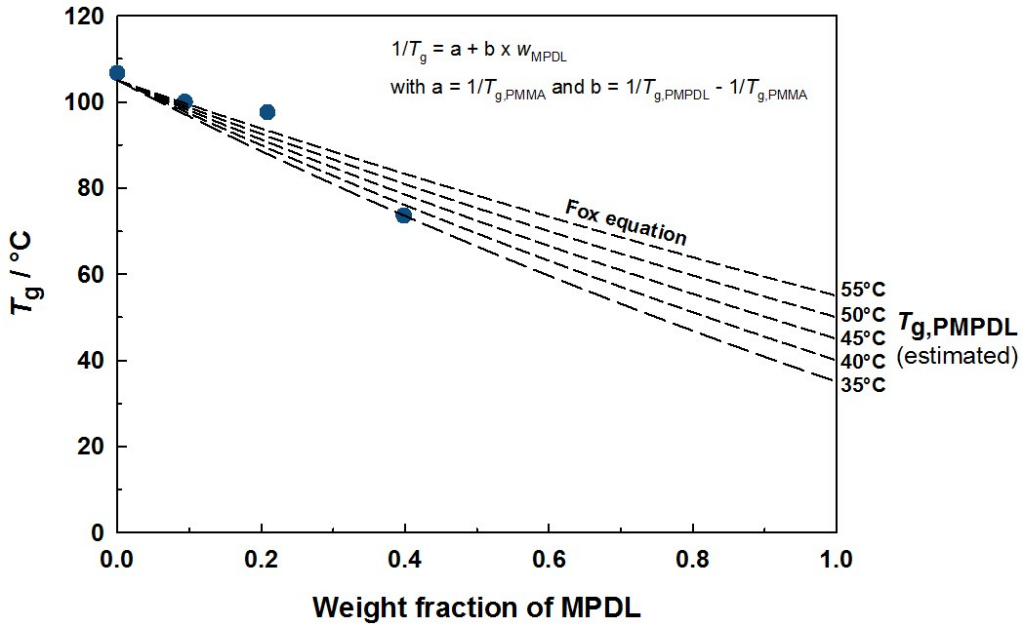

Figure S7. Experimental T_g values of the different copolymers as function of the weight fraction of MPDL in the copolymer, and curve of the Fox equation[2] ($1/T_g = w_{PMPDL}/T_{g,PMPDL} + w_{MMA}/T_{g,PMMA}$, with w and T_g the weight fraction and T_g of each homopolymer) with an estimated T_g for PMDPL of 45 ± 10 °C.

References

1. Van Den Brink, M.; Van Herk, A. M.; German, A. L. *J. Polym. Sci., Part A: Polym. Chem.* **1999,** 37, 3793-3803.
2. Fox, T. G. *Bull. Am. Phys. Soc.* **1956,** 1, 123-125.