Supporting Information

Lowering ketene formation temperature in polymer systems through molecular engineering

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Contents:

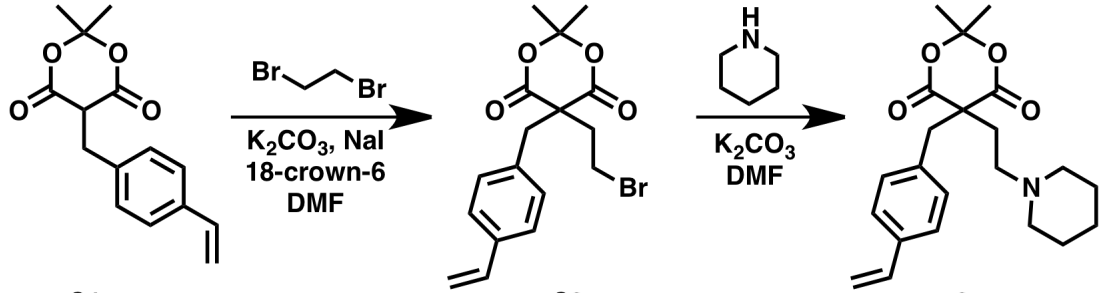
General Methods:

All commercially obtained solvents and reagents were used without further purification. 2,2-dimethyl-5-(4-vinylbenzyl)-1,3-dioxane-4,6-dione,[1] 5-benzyl-2,2-dimethyl-1,3-dioxane-4,6-dione,[2] 5-benzyl-2,2-dimethyl-5-(4-vinylbenzyl)-1,3dioxane-4,6-dione[2] 5-(4-hydroxybenzyl)-2,2,5-trimethyl-1,3-dioxane-4,6-dione,[3] and 5-(4-(hydroxymethyl)benzyl)-2,2,5-trimethyl-1,3-dioxane-4,6-dione[3] were prepared according to literature procedures. Analytical thin-layer chromatography (TLC) was carried out on Merck silica gel 60 F_{254} glass plates and flash column chromatography was performed on Merck silica gel 60 (70 – 230 mesh) or on a Biotage SP1 Flash Purification System using FLASH 40+M cartridges and FLASH 40+ sample cartridges. ^{1}H and ^{13}C solution-state NMR were recorded on a Varian VNMRS 600 (600 MHz for ^{1}H and 150 MHz for ^{13}C) spectrometer or Varian Inova-500 (500 MHz for ^{1}H, and 125 MHz for ^{13}C). Chemical shifts are reported relative to residual solvent peaks (δ 7.26 for $CDCl_3$ or δ 2.50 for DMSO-d_6 in ^{1}H NMR and δ 77.2 for $CDCl_3$ or δ 39.52 for DMSO-d_6 in ^{13}C NMR). IR spectra were obtained using a Thermo-Nicholet Avatar-330 IR spectrometer with [1]single-bounce attenuated total reflection (ATR) (Ge crystal) accessory (Smart MIRacle). Gel permeation chromatography (GPC) was performed in chloroform (with 0.25% triethylamine) on a Waters 2695 Separation Module equipped with a Waters 2414 Refractive Index Detecter and a Waters 2996 Photodiode Array Detector. Molecular weights of polymers were calculated relative to linear polystyrene standards. Differential scanning calorimetry (DSC) data was aquired on a TA Instruments Q2000 modulated DSC at a heating rate of 5 °C/min. Data presented are from the second heating after a single cycle from -25 to 180 °C. Mass spectral data were collected on a Micromass QTOF2 Quadrupole/Time-of Flight Tandem mass spectrometer (ESI-MS). TGA and TGA-MS data were collected on a Mettler 851e TG coupled with a Pfeiffer ThermoStar Mass Spectrometer.

Computational Methods:

We study the lowering of ketene formation temperature using transition-state density functional calculations with the Gaussian 03 software package.[4] Our calculations employed the B3LYP exchange-correlation functional[5] and the 6-31G(d) basis set.[6] We find the transition-state barrier for ketene formation through a concerted mechanism to be 40.8 kcal/mol and 37.5 kcal/mol in the presence and absence of hydroxyl interactions, respectively. We have verified that the transition state in each case has exactly one imaginary-frequency vibrational mode, and that this mode corresponds to simultaneous separation of ketene and CO_2 fragments.

Synthetic Methods:



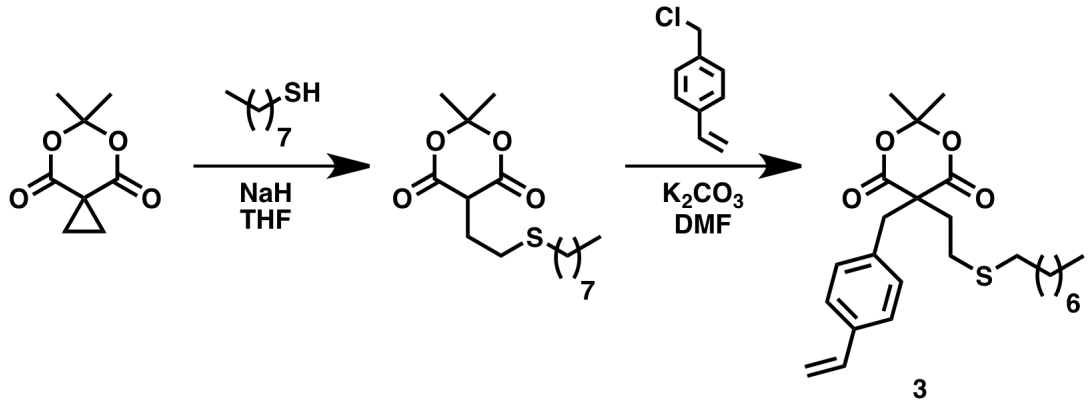
S1 S2 2

5-(2-bromoethyl)-2,2-dimethyl-5-(4-vinylbenzyl)-1,3-dioxane-4,6-dione (S2): To a dry 50 mL round bottom flask equipped with a stir bar, **S1** (1.00 g, 3.84 mmol), 1,2-dibromoethane (4.14 g, 22.0 mmol), DMF (3 mL), 18-crown-6 (3 mg, 0.01 mmol), and K_2CO_3 (960 mg, 6.96 mmol), were combined. The reaction mixture was allowed to stir at 50 °C for three days. The reaction was quenched into 100 mL of 1 N HCl, extracted ×3 with 30 mL Et_2O, the organic phases were combined and washed with brine, dried over $MgSO_4$, and concentrated. The mixture was purified by flash column chromotagraphy (5 % EtOAc:Hex) to afford the product as a crystalline solid (590 mg, 42 % yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, *J*=7.8 Hz, 2H), 7.13 (d, *J*=7.8 Hz, 2H), 6.64 (dd, *J*=10.8 and 17.4 Hz, 1H), 5.71 (d, *J*=17.4 Hz, 1H), 5.23 (d, *J*=10.8 Hz, 1H), 3.34 (t, *J*=7.8 Hz, 2H), 3.32 (s, 2H), 2.73 (t, *J*=7.8 Hz, 2H), 1.61 (s, 3H), 0.72 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.0, 137.7, 136.3, 134.1, 130.8, 126.9, 114.7, 106.7, 56.8, 44.2, 42.6, 29.6, 29.1, 25.8; IR (ATR) 3104, 3033, 2997, 2949, 2875, 1765, 1730, 1633, 1512, 1449, 1391, 1362, 1278, 1228, 1203, 1093, 917, 852, 703 cm^{-1}; MS (TOF-ESI) calcd for $C_{17}H_{19}BrO_4Na$ [M+Na]: 389.05, [2M+Na]: 755.10. Found: [M+Na]: 389.05, 391.05 [2M+Na]: 755.10, 757.09, 759.11.

2,2-dimethyl-5-(2-(piperidin-1-yl)ethyl)-5-(4-vinylbenzyl)-1,3-dioxane-4,6-dione (2): To a dry 50 mL round bottom flask equipped with a stir bar, **S2** (300 mg, 0.82 mmol), DMF (5 mL), piperidine (68 mg, 0.80 mmol), K_2CO_3 (193 mg, 1.4 mmol) were combined and allowed to stir at room temperature for 2 days at 50 °C. The reaction was quenched with 75 mL 1 N HCl and extracted ×2 with EtOAc. The aqueous layer was subsequently made basic by addition of a saturated solution of $NaHCO_3$ and that aqueous layer was extracted ×3 with 40 mL Et_2O. The Et_2O layers were combined, washed with brine and dried over Na_2SO_4. The solvent was removed to provide the desire product as a crystalline solid (205 mg, 67 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J*=8.0 Hz, 2H), 7.12 (d, *J*=8.0 Hz, 2H), 6.63 (dd, *J*=11.0 and 18.0 Hz, 1H), 5.69 (d, *J*=17.5 Hz, 1H), 5.21 (d, *J*=11.0 Hz, 1H), 3.23 (s, 2H), 2.40-2.1 (m, 8H), 1.60 (s, 3H), 1.52-1.25 (m, 6H), 0.65 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 137.4, 136.4, 134.7, 130.6, 126.7, 114.4, 106.2, 68.4, 55.4, 54.8, 46.2, 36.5, 29.3, 28.9, 25.6, 24.6; HR-MS (TOF-ESI) calcd for $C_{22}H_{29}NO_4$ [M+H] 372.21, [M+Na]: 394.21. Found: [M+H] 372.24, [M+Na]: 394.23.

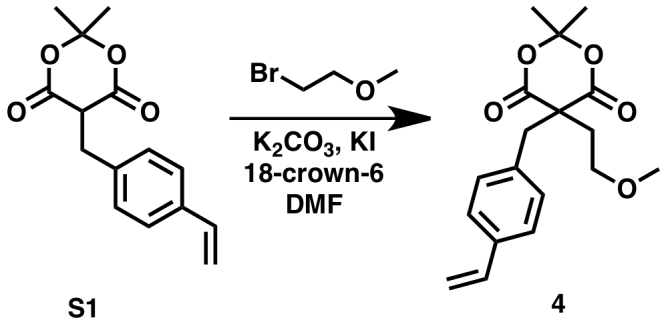
Crystal data for 2: Crystals suitable for analysis were grown by slow cooling of **2** in 3 % EtOAc:Hex solution. $C_{22}H_{29}NO_4$ Unit Cell: a = 16.339(3) Å, b = 7.8427(14) Å, c = 16.851(3) Å, β = 108.538(3) °, V = 2054.7(6) Å^3, Z = 4, T = 293 (2) K, ρ_{calc} = 1.201

g/cm^3, μ = 0.082 mm^{-1}, *F(000)* = 800, A total of 15914 reflections were collected, of which 4134 were unique (R_{int} = 0.0964). (shown in text)

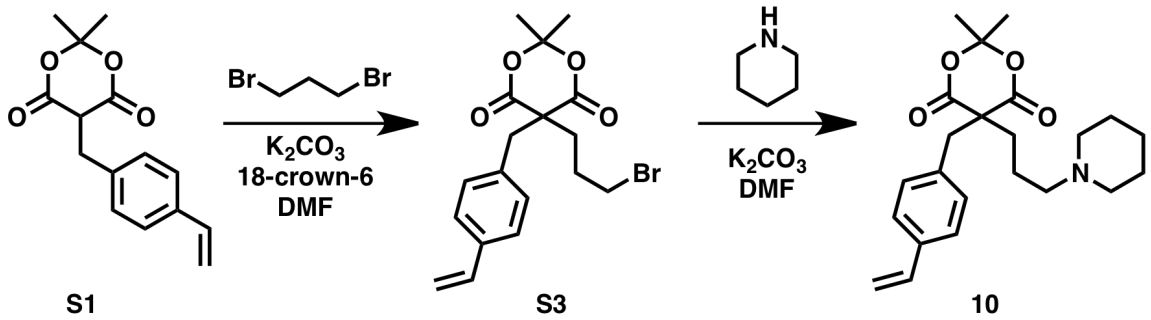


2,2-dimethyl-5-(2-(octylthio)ethyl)-5-(4-vinylbenzyl)-1,3-dioxane-4,6-dione (3): To a dry 250 mL round bottom flask equipped with a stir bar, dry THF (120 mL) and sodium hydride (352 mg 60 wt. % dispersion in mineral oil, 8.82 mmol) were added under an argon atmosphere. The slurry was cooled to 0 °C and octane thiol (1.29 g, 8.82 mmol) was added dropwise. The solution was warmed to room temperature and allowed to stir for 30 minutes. The resulting thiolate solution was cannula transferred to a solution of cyclopropyl Meldrum's acid (1.50 g, 8.82 mmols) in 20 mL dry THF under an inert atmosphere at -78 °C. Upon completion of transfer, the solution was slowly warmed to 0 °C and subsequently room temperature and allowed to stir overnight. The reaction was quenched with 1 N HCl and the aqueous fraction was extracted ×3 with EtOAc, the organic phases were combined, washed with brine, and dried over $MgSO_4$. A short plug of silica was used to remove any excess octane thiol.

The resulting white solid (335 mg) was added to a dry 50 mL round bottom flask equipped with a stir bar and dry DMF (8 mL), 1-(chloromethyl)-4-vinylbenzene (183 mg, 1.2 mmol), and K_2CO_3 (276 mg, 2 mmol) were added. The solution was set at 50 °C to stir for 16 hours. The reaction was quenched with 1 N HCl and the aqueous phase was extracted ×3 with Et_2O, the organic phases were combined, washed with brine, and dried over $MgSO_4$. The desired product (**3**) was purified by flash column chromatography on silica gel (0 to 5 % EtOAc:Hex) to afford a clear oil (205 mg, 6 % yield over two steps). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J*=6.0 Hz, 2H), 7.13 (d, *J*=8.4 Hz, 2H), 6.63 (dd, *J*=10.8 and 18.0 Hz, 1H), 5.69 (d, *J*=17.4 Hz, 1H), 5.22 (d, *J*=10.8 Hz, 1H), 3.29 (s, 2H), 2.49 (t, *J*=7.2 Hz, 2H), 2.44 (m, 4H), 1.59 (s, 3H), 1.54 (m, 2H), 1.36-1.25 (m, 10H), 0.87 (t, *J*=6.6 Hz, 3H), 0.69 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.3, 136.2, 135.1, 133.4, 129.5, 125.6, 113.3, 105.3, 55.8, 43.2, 39.1, 30.8, 28.3, 28.3, 28.2, 28.1, 27.9, 27.8, 26.2, 21.6, 13.1; HR-MS (TOF-ESI) calcd for $C_{21}H_{30}O_4SNa$ [M+Na]: 455.23, [2M+Na]: 887.46. Found: [M+Na]: 455.23, [2M+Na]: 887.48.



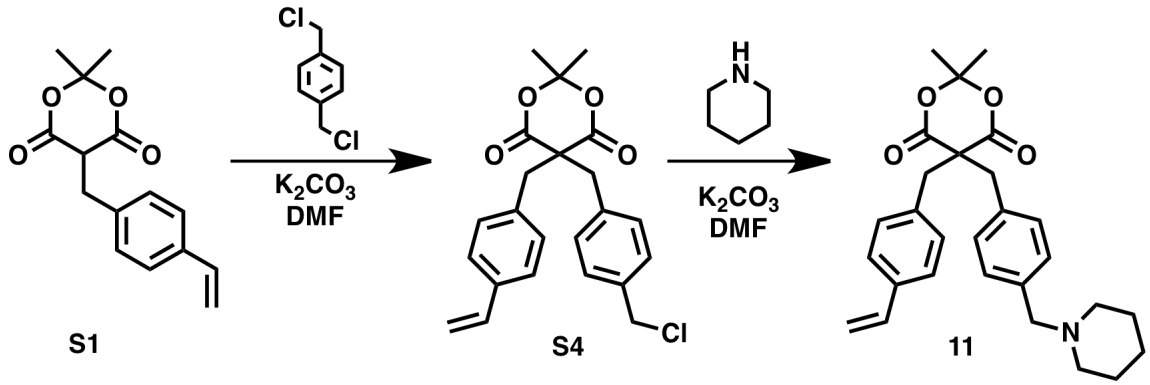
5-(2-methoxyethyl)-2,2-dimethyl-5-(4-vinylbenzyl)-1,3-dioxane-4,6-dione (4): To a dry 50 mL round bottom flask equipped with a stir bar, **S1** (900 mg, 3.45 mmol), 1-bromo-2-methoxyethane (715 mg, 5.18 mmol), DMF (3 mL), potassium iodide (687 mg, 4.14 mmol), K_2CO_3 (690 mg, 5 mmol), and 18-crown-6 (5 mg, 0.02 mmol) were combined. The reaction mixture was allowed to stir at 50 °C for three days. The reaction was quenched into 100 mL of 1 N HCl, extracted ×3 with 30 mL Et_2O, the organic phases were combined and washed with brine, dried over $MgSO_4$, and concentrated. The mixture was purified by flash column chromotagraphy (10 to 15 % EtOAc:Hex) to afford the product as a white solid (445 mg, 40 % yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, *J*=7.8 Hz, 2H), 7.14 (d, *J*=8.4 Hz, 2H), 6.65 (dd, *J*=10.8 and 17.4 Hz, 1H), 5.71 (d, *J*=18 Hz, 1H), 5.22 (d, *J*=11.4 Hz, 1H), 3.46 (t, *J*=5.4 Hz, 2H), 3.27 (s, 2H), 3.25 (s, 3H), 2.49 (t, *J*=6 Hz, 2H), 1.57 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 137.3, 136.2, 134.2, 130.4, 126.6, 114.2, 106.3, 68.3, 58.4, 54.1, 45.9, 38.6, 28.7, 28.6; HR-MS (TOF-ESI) calcd for $C_{18}H_{22}O_5Na$ [M+Na]: 341.15, [2M+Na]: 659.3 Found: [M+Na]: 341.28, [2M+Na]: 659.46.



5-(3-bromopropyl)-2,2-dimethyl-5-(4-vinylbenzyl)-1,3-dioxane-4,6-dione (S3): To a dry 50 mL round bottom flask equipped with a stir bar, **S1** (921 mg, 3.53 mmol), 1,2-dibromoethane (3.63 g, 18.0 mmol), DMF (3 mL), 18-crown-6 (3 mg, 0.01 mmol), and K_2CO_3 (828 mg, 6.00 mmol), were combined. The reaction mixture was allowed to stir at 50 °C for three days. The reaction was quenched into 100 mL of 1 N HCl, extracted ×3 with 30 mL Et_2O, the organic phases were combined and washed with brine, dried over $MgSO_4$, and concentrated. The mixture was purified by flash column chromotagraphy (5 % EtOAc:Hex) to afford the product as a crystalline solid (560 mg, 42 % yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J*=8.4 Hz, 2H), 7.13 (d, *J*=7.8 Hz, 2H), 6.64 (dd, *J*=10.8 and 17.4 Hz, 1H), 5.69 (d, *J*=18 Hz, 1H), 5.22 (d, *J*=10.8 Hz, 1H), 3.36 (t, *J*=6.6 Hz, 2H), 3.32 (s, 2H), 2.28 (m, 2H), 1.87 (m, 2H), 1.57 (s, 3H), 0.72 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.8, 137.5, 136.3, 134.7, 130.8, 126.8, 114.5, 106.3, 57.1, 43.7, 39.7, 31.7,

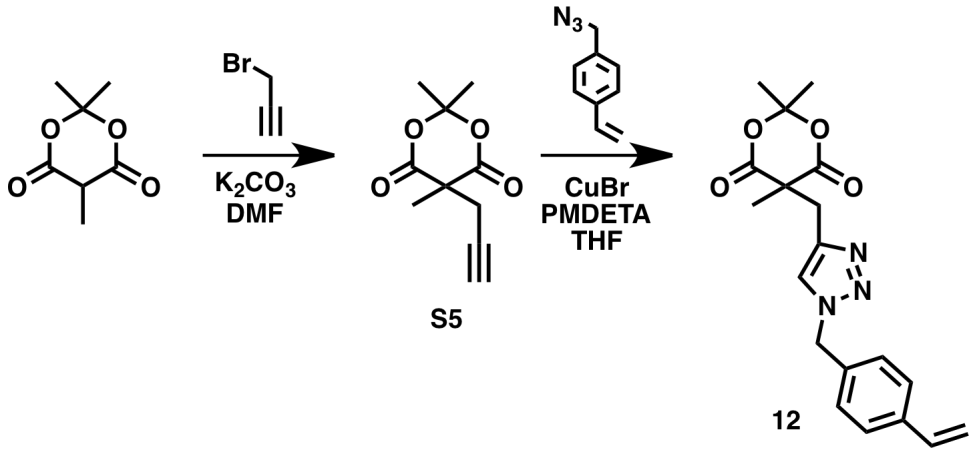
29.7, 29.2, 28.7; IR (ATR) 3086, 3006, 2967, 2938, 2854, 1775, 1733, 1629, 1510, 1447, 1378, 1344, 1268, 1247, 1202, 933, 845, 698 cm^{-1}; HRMS (TOF-ESI) calcd for $C_{17}H_{19}BrO_4Na$ [M+Na]: 403.06, [2M+Na]: 783.12. Found: [M+Na]: 403.05, 405.06 [2M+Na]: 783.12, 785.13, 787.12.

2,2-dimethyl-5-(3-(piperidin-1-yl)propyl)-5-(4-vinylbenzyl)-1,3-dioxane-4,6-dione (10): To a dry 50 mL round bottom flask equipped with a stir bar, **24** (230 mg, 0.60 mmol), DMF (5 mL), piperidine (51 mg, 0.60 mmol), K_2CO_3 (138 mg, 1.0 mmol) were combined and allowed to stir at room temperature for 2 days at 50 °C. The reaction was quenched with 75 mL 1 N HCl and extracted ×2 with EtOAc. The aqueous layer was subsequently made basic by addition of a saturated solution of $NaHCO_3$ and that aqueous layer was extracted 3×40 mL Et_2O. The Et_2O layers were combined, washed with brine and dried over Na_2SO_4. The solvent was removed to provide the desired product as a clear oil (208 mg, 89 % yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, *J*=8.4 Hz, 2H), 7.13 (d, *J*=7.8 Hz, 2H), 6.63 (dd, *J*=10.8 and 17.4 Hz, 1H), 5.69 (d, *J*=17.4 Hz, 1H), 5.21 (d, *J*=10.8 Hz, 1H), 3.30 (s, 2H), 2.35-2.27 (m, 6H), 2.15 (m, 2H), 1.58-1.52 (m, 7H), 1.50-1.38 (m, 4H), 0.70 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.1, 137.3, 136.4, 135.2, 130.7, 126.8, 114.4, 106.1, 58.6, 57.6, 54.7, 43.7, 39.3, 29.7, 29.2, 26.1, 24.6, 23.0; HR-MS (TOF-ESI) calcd for $C_{23}H_{31}NO_4H$ [M+H]: 386.2331 Found: [M+H]: 386.2320



2,2-dimethyl-5-(2-(4-(chloromethyl)benzyl)-5-(4-vinylbenzyl)-1,3-dioxane-4,6-dione (S4): To a dry 25 mL round bottom flask equipped with a stir bar, **S1** (500 mg, 1.92 mmol, 1 eq), DMF (5 mL), 1,4-bis(dichloromethyl)benzene (1.01 g, 5.76 mmol, 3eq), K_2CO_3 (538 mg, 3.84 mmol, 2 eq) were combined and allowed to stir at 50 °C for 17 hrs. The reaction was quenched with 100 mL 1 N HCl and extracted ×3 with 50 mL EtOAc. The combined organic layer was dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was purified by by flash column chromotagraphy (20 to 40% DCM in hexanes) yielding **S4** as a white solid (405 mg, 53 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J*=8.0 Hz, 2H), 7.31 (d, *J*=8.0 Hz, 2H), 7.20 (d, *J*=8.0 Hz, 2H), 7.16 (d, *J*=8 Hz, 2H), 6.64 (dd, *J*=15 and 10 Hz, 1H), 5.70 (d, *J*=15 Hz, 1H), 5.22 (d, *J*= 10 Hz, 1H) 4.52 (s, 2H), 3.45 (s, 2H), 3.44 (s, 2H), 0.68 (s, 3H), 0.66 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 137.3, 137.1, 136.1, 135.1, 134.2, 130,5. 130.3, 129.1, 126.6, 114.2, 106.1, 59.9, 45.7, 44.6, 44.5, 28.7; HR-MS (TOF-ESI) calcd for $C_{23}H_{23}ClO_4Na$ $[M+Na]^+$ 421.118 Found: $[M+Na]^+$ 421.117.

2,2-dimethyl-5-(4-(piperidin-1-yl)benzyl)-5-(4-vinylbenzyl)-1,3-dioxane-4,6-dione (11): To a dry 25 mL round bottom flask equipped with a stir bar, **S4** (405 mg, 1.01 mmol, 1 eq), DMF (5 mL), piperidine (86 mg, 1.0 mmol, 1eq), K_2CO_3 (213 mg, 1.52 mmol, 1.5 eq) were combined and allowed to stir at 50 °C for 17 hrs. The reaction was quenched with 20 mL 1 N HCl and extracted ×3 with Et_2O (50 mL each). The aqueous layer was made basic by addition of $NaHCO_3$ and subsequently extracted ×3 with EtOAc (50 mL each). The EtOAc layer was washed 6 times with saturated aqueous $NaHCO_3$ solution, dried with Na_2SO_4, filtered and the solvent was evaporated yielding **11** as a white solid (314 mg, 69 % yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, *J*=12 Hz, 2H), 7.22 (d, *J*=12 Hz, 2H), 7.17 (d, *J*=6.0 Hz, 2H), 7.14 (d, *J*=12 Hz, 2H), 6.64 (dd, *J*=18 and 12 Hz, 1H), 5.70 (d, *J*=18 Hz, 1H), 5.21 (d, *J*= 12 Hz, 1H) 4.52 (s, 2H), 3.44 (2 s, 4H), 3.41 (s, 2H), 2.29 (m, 4H), 1.54-1.49 (m, 4H), 1.40-1.34 (m, 2H), 0.70 (s, 3H) 0.63 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 136.2, 135.3, 133.5, 129.6, 129.1, 125.9, 113.9, 105.9, 64.6, 61.5, 55.9, 46.7, 46.5, 31.1, 28.3, 26.8; HR-MS (TOF-ESI) calcd for $C_{28}H_{34}NO_4$ $[M]^+$ 448.249 Found: $[M]^+$ 448.247.

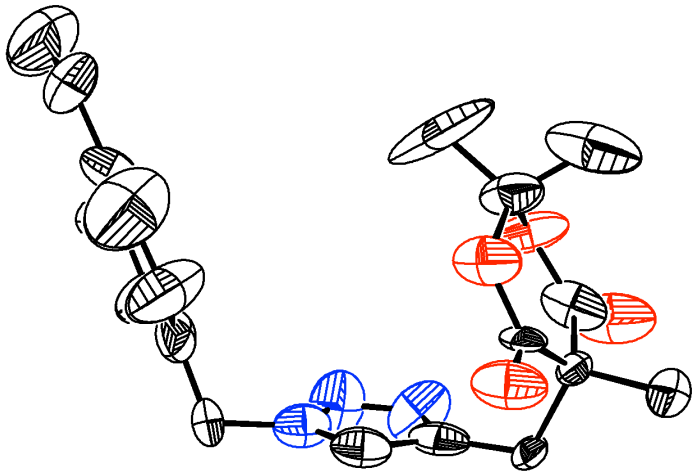


2,2-dimethyl-5-(prop-2-yn-1-yl)-1,3-dioxane-4,6-dione (S5): To a dry 50 mL round bottom flask equipped with a stir bar, 2,2,5-trimethyl-1,3-dioxane-4,6-dione (5.0 g, 31.7 mmol), propargyl bromide (5.65 g of 80 wt. % solution in toluene, 38.0 mmol), DMF (20 mL), and K_2CO_3 (7.86 g, 57.0 mmol), were combined. The reaction mixture was allowed to stir at room temperature for 5 hours. The reaction was quenched into 150 mL of 1 N HCl, extracted ×3 with 50 mL Et_2O, the organic phases were combined and washed with brine, dried over $MgSO_4$, and concentrated. The mixture was purified by flash column chromotagraphy (5 % EtOAc:Hex) to afford the product as a crystalline solid (4.68 g, 75 % yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.88 (d, *J*=2.4 Hz, 2H), 2.10 (t, *J*=2.4 Hz, 1H), 1.79 (s, 3H), 1.75 (s, 3H), 1.62 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.0, 105.6, 78.4, 72.4, 49.6, 29.4, 29.2, 28.2, 24.9; IR (ATR) 3297, 3007, 2971, 2965, 1769, 1737, 1456, 1385, 1323, 1277, 1202, 1140, 1056, 982, 942, 725, 694, 677 cm^{-1}; HR-MS (TOF-ESI) calcd for [M+]: 196.0736. Found: [M+]: 196.0745.

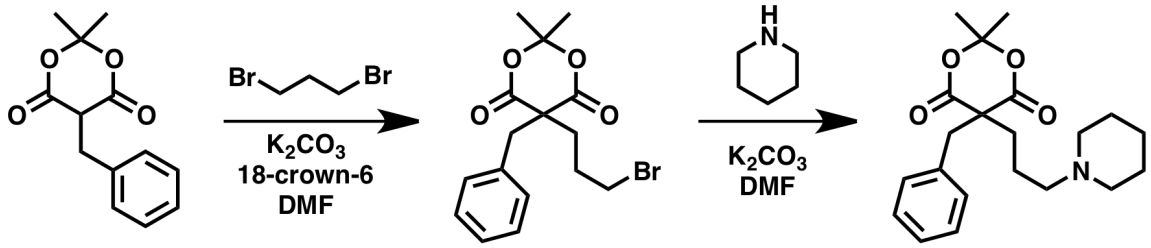
2,2,5-trimethyl-5-((1-(4-vinylbenzyl)-1*H*-1,2,3-triazol-4-yl)methyl)-1,3-dioxane-4,6-dione (12): To a 3-neck, 100 mL roundbottom flask equipped with a stir bar, 1-

(azidomethyl)-4-vinylbenzene (1.00 g, 6.29 mmol), **S5** (1.23 g, 6.29 mmol), and N,N,N',N'',N''-pentamethyldiethylenetriamine (109 mg, 0.63 mmol), were combined in 20 mL THF. Argon was subsequently bubbled through the solution for 20 minutes, at which time CuBr (92 mg, 0.63 mmol) was added under an inert atmosphere. Argon was bubbled for another 10 minutes. The reaction was stirred for 20 hours at 50 °C. The reaction mixture was subsequently quenched into 100 mL H_2O, extracted ×3 with 40 mL EtOAc, the organic fractions were combined and washed with brine and dried over $MgSO_4$. The solvent was evaporated and the white solid was recrystallized in 60 % EtOAc:Hex to afford the product as a crystalline solid (2.15 g, 96 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J*=8.5 Hz, 2H), 7.15 (d, *J*=8.5 Hz, 2H), 6.65 (dd, *J*=10.5 and 17.5 Hz, 1H), 5.72 (d, *J*=17.5 Hz, 1H), 5.40 (s, 2H), 5.24 (d, *J*=10.5 Hz, 1H), 3.40 (s, 2H), 1.70 (s, 3H), 1.69 (s, 3H) 1.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 142.6, 138.0, 136.0, 134.0, 128.3, 126.8, 122.0, 114.9, 105.9, 68.3, 53.8, 49.0, 34.1, 29.5, 28.5, 25.7; IR (ATR) cm^{-1} 3132, 3013, 2997, 2944, 1780, 1734, 1514, 1458, 1447, 1383, 1328, 1206, 1128, 1057, 982, 938, 904, 797; HR-MS (TOF-ESI) calcd for $C_{19}H_{21}N_3O_4$ [M+H] 356.15, [2M+Na]: 733.30. Found: [M+H] 356.17, [2M+Na]: 733.33.

Crystal data for 12: Crystals suitable for analysis were grown by slow cooling of **12** in hexane. $C_{19}H_{21}N_3O_4$ *Iba2*, Unit Cell: a = 17.443(4) Å, b = 21.703(5) Å, c = 9.844(2) Å, β = 90 °, V = 3726.8(15) Å^3, Z = 8, T = 293 (2) K, ρ_{calc} = 1.267 g/cm^3, μ = 0.090 mm^{-1}, *F(000)* = 1504, A total of 9632 reflections were collected, of which 3477 were unique (R_{int} = 0.1257).



ORTEP diagram of crystal structure of **12** displaying 50% ellipsoids.

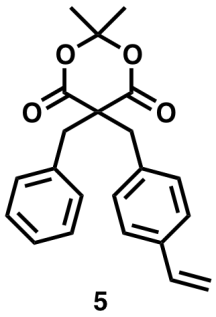


S7 S8 S9

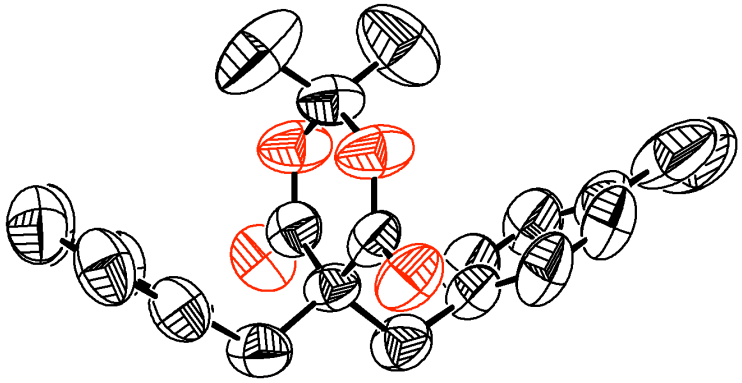
5-benzyl-5-(3-bromopropyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (S8): To a dry 50 mL round bottom flask equipped with a stir bar, 5-benzyl-2,2-dimethyl-1,3-dioxane-4,6-dione (**S7**) (921 mg, 3.53 mmol), 1,2-dibromoethane (3.63 g, 18.0 mmol), DMF (3 mL), 18-crown-6 (3 mg, 0.01 mmol), and K_2CO_3 (828 mg, 6.00 mmol), were combined. The reaction mixture was allowed to stir at 50 °C for three days. The reaction was quenched into 100 mL of 1 N HCl, extracted ×3 with 30 mL Et_2O, the organic phases were combined and washed with brine, dried over $MgSO_4$, and concentrated. The mixture was purified by flash column chromotagraphy (5 % EtOAc:Hex) to afford the product as a crystalline solid (560 mg, 42 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (m, 3H), 7.18 (d, *J*=8.5 Hz, 2H), 3.36 (t, *J*=6.5 Hz, 2H), 3.33 (s, 2H), 2.29 (m, 2H), 1.86 (m, 2H), 1.56 (s, 3H), 0.63 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.8, 135.3, 130.6, 129.2, 128.2, 106.3, 57.2, 43.9, 39.8, 31.8, 29.7, 29.0, 28.7; IR (ATR) 3078, 3039, 2997, 2939, 2856, 1766, 1729, 1496, 1446, 1392, 1378, 1339, 1266, 1246, 1203, 1102, 1078, 944, 701 cm^{-1}; HR-MS (TOF-ESI) calcd for $C_{17}H_{19}BrO_4Na$ [M+Na]: 377.05, [2M+Na]: 733.10. Found: [M+Na]: 377.04, 379.04 [2M+Na]: 731.08, 733.09, 735.08

5-benzyl-2,2-dimethyl-5-(3-(piperidin-1-yl)propyl)-1,3-dioxane-4,6-dione (S9): To a dry 50 mL round bottom flask equipped with a stir bar, **S8** (220 mg, 0.620 mmol), K_2CO_3 (165 mg, 1.20 mmol), piperidine (53 mg, 0.620 mmols), and dry DMF (5 mL) were added and allowed to stir for 48 hours. The reaction mixture was quenched with 100 mL sat. sodium bicarbonate and extracted ×3 with Et_2O, the organic phases were combined and washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by recrystallization from ~2% EtOAc:Hex by slow cooling to afford the product as transparent crystals (105 mg, 47 % yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.32-7.29 (m, 3H), 7.06 (d, *J* = 7 Hz, 2H), 3.23 (s, 2H), 2.23-2.15 (m, 6H), 2.10-2.02 (m, 2H), 1.53 (s, 3H), 1.49-1.44 (m, 4H), 1.39-1.31 (m, 4H), 0.63 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 168.3, 135.3, 129.9, 128.8, 127.4, 105.7, 57.4, 56.8, 53.8, 29.0, 28.8, 28.7, 28.5, 25.5, 24.1, 22.7.

Crystal data for S9: Crystals suitable for analysis were grown by slow cooling of **S9** in hexane. $C_{21}H_{29}NO_4$ *P2(1)/n*, Unit Cell: *a* = 11.210(5) Å, *b* = 16.029(7) Å, *c* = 11.499(5) Å, β = 102.731(7) °, *V* = 2015.5(15) Å^3, *Z* = 4, *T* = 293 (2) K, ρ_{calc} = 1.185 g/cm^3, μ = 0.081 mm^{-1}, *F(000)* = 776, A total of 15829 reflections were collected, of which 4031 were unique (R_{int} = 0.0665). (shown in text)

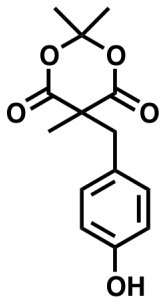


5



ORTEP diagram of crystal structure of **5** displaying 50% ellipsoids.

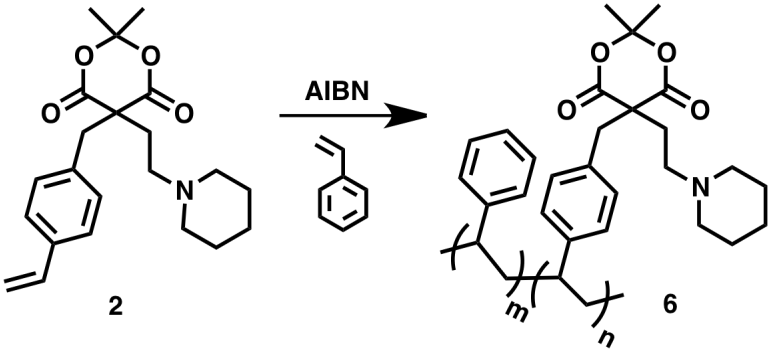
Crystal data for 5: Crystals suitable for analysis were grown by slow cooling of **5** in 5 % EtOAc:Hex. $C_{22}H_{22}O_4$ *P2(1)/c*, Unit Cell: a = 9.534(2) Å, b = 19.600(5) Å, c = 10.977(3) Å, β = 110.365(3) °, V = 1923.0(8) Å^3, Z = 4, T = 293 (2) K, ρ_{calc} = 1.210 g/cm^3, μ = 0.083 mm^{-1}, *F(000)* = 744, A total of 13767 reflections were collected, of which 3575 were unique (R_{int} = 0.1455).



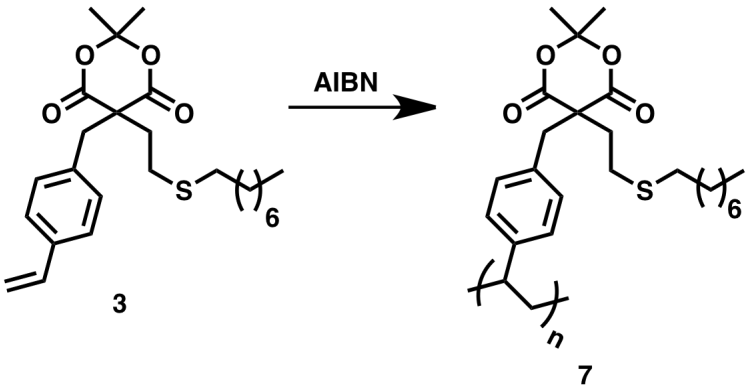
16

Crystal data for 16: Crystals suitable for analysis were grown by controlled vapor diffusion method of diethyl ether to a solution of **16** in DCM. $C_{14}H_{16}O_5$ *Monoclinic, P2(1)/n*, Unit Cell: a = 14.348(5) Å, b = 11.622(4) (5) Å, c = 16.672(6) Å, β = 103.442(5) °, V = 2703.8(17) Å^3, Z = 8, T = 293 (2) K, ρ_{calc} = 1.298 g/cm^3, μ = 0.099 mm^{-1}, *F(000)* = 1120, A total of 20563 reflections were collected, of which 5350 were unique (R_{int} = 0.0321). (shown in text)

Polymer synthesis

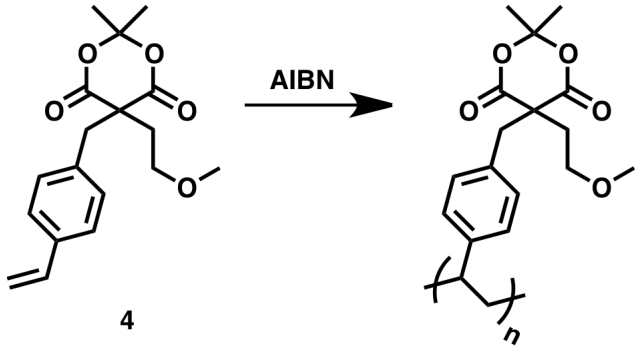


General free-radical polymerization procedure to afford polymer 6: Following the general procedure outlined above, **2** (160 mg, 0.431 mmol), styrene (404 mg, 3.88 mmol), azobisisobutyronitrile (AIBN) (5 mg, 0.0304 mmol), and chlorobenzene (3 mL) were combined. The solution was deoxygenated by freezing in liquid nitrogen under vacuum and subsequent thawing at room temperature. This process was repeated three times, upon which the vessel was placed in an oil bath and heated to 65 °C for 16 hours.The reaction mixture was cooled, precipitated into 125 mL MeOH and purified by preparatory GPC with $CHCl_3$ as an eluent, concentrated, and precipitated into 100 mL MeOH to recover the desired polymer as a white powder (80 mg, 14 %). ^{1}H NMR (600 MHz, $CDCl_3$) 7.2-6.2 (m, 54H), 3.3-3.1 (br s, 2H), 2.5-2.2 (m, 8H), 2.2-1.0 (m, 49H), 0.8-0.1 (m, 3H). IR (ATR) 3104, 3031, 2997, 2877, 1766, 1733, 1512, 1449, 1388, 1362, 1274, 1274, 1093, 917, 852, 703 GPC M_n= 18.2 kg mol^{-1}, M_w= 34.9 kg mol^{-1}, PDI = 1.92.

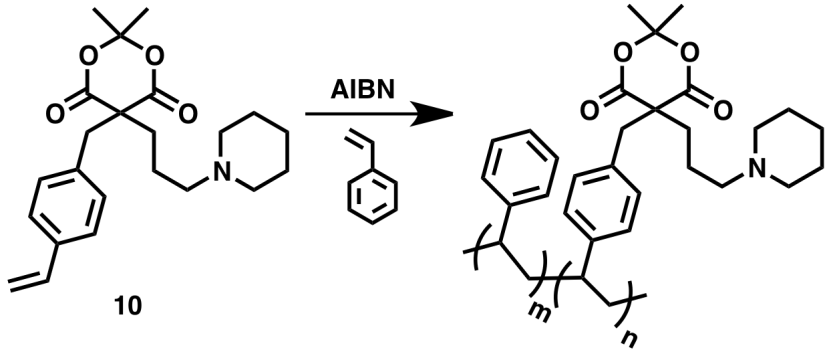


Polymerization of 3: Following the general procedure outlined above, **3** (205 mg, 0.474 mmol), azobisisobutyronitrile (AIBN) (3 mg, 0.0183 mmol), and chlorobenzene (1.50 mL) were combined and reacted. The reaction mixture was cooled, precipitated into 125 mL MeOH and purified by preparatory GPC with $CHCl_3$ as an eluent, concentrated, and precipitated into 100 mL MeOH to recover the desired polymer as a white powder (110 mg, 54 %). ^{1}H NMR (600 MHz, $CDCl_3$) δ7.2-6.9 (br m, 4H), 3.4-3.0 (br s, 2H), 2.5-2.1

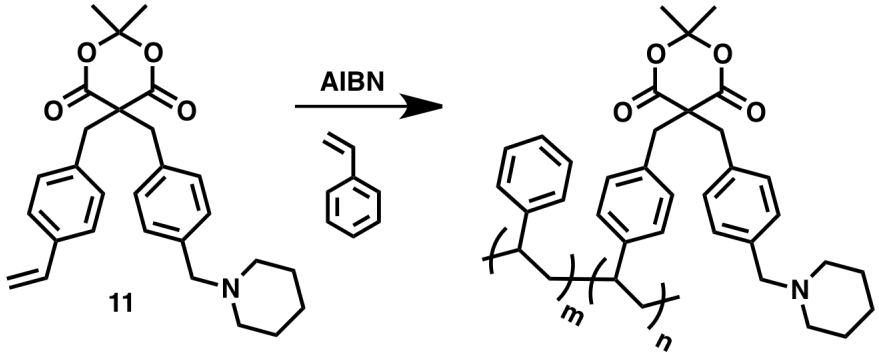
(m, 6H), 1.6-1.0 (m, 18H), 0.82-0.70 (br s, 3H), 0.60-.02 (br s, 3H); IR (ATR) 3034, 3004, 2928, 2856, 1774, 1738, 1513, 1446, 1380, 1362, 1274, 1205, 1049, 953, 730 cm^{-1}; GPC M_n= 23.0 kg mol^{-1}, M_w= 56.0 kg mol^{-1}, PDI=2.40; DSC: no thermal transitions evident between -20-150 °C.



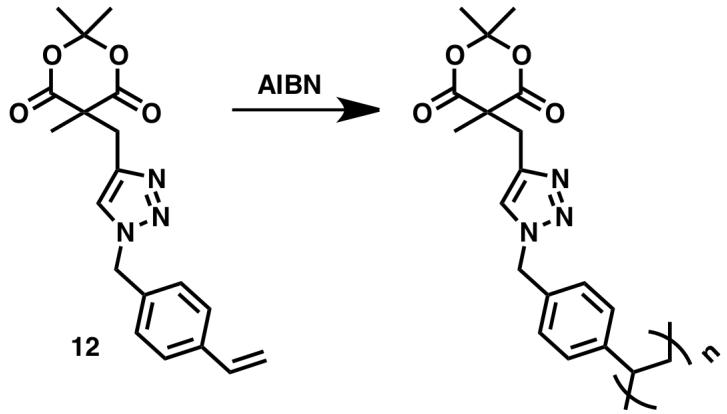
Polymerization of 4: Following the general procedure outlined above, **4** (220 mg, 0.691 mmol), AIBN (3 mg, 0.0183 mmol), and DMF (1.50 mL) were combined and reacted. The resulting polymer was precipitated twice into 125 mL of cold Et_2O to recover the desired polymer as a white powder (80 mg, 36 %). ^{1}H NMR (600 MHz, $CDCl_3$) 7.1-6.2 (br m, 4H), 3.5-3.4 (br t, 2H), 3.3-3.1 (m, 5H), 2.6-2.4 (br t, 2H), 1.8-0.8 (m, 6H), 0.7-0.2 (br s, 3H); GPC M_n= 26.2 kg mol^{-1}, M_w= 57.9 kg mol^{-1}, PDI = 2.21.



Polymerization of 10: Following the general procedure outlined above, **10** (205 mg, 0.53 mmol), styrene (110 mg, 1.06 mmol), AIBN (3 mg, 0.0183 mmol), and chlorobenzene (1.5 mL) were combined and reacted. The reaction mixture was cooled, precipitated into 125 mL MeOH and purified by preparatory GPC with $CHCl_3$ as an eluent, concentrated, and precipitated into 40 mL MeOH to recover the desired polymer as a white powder (40 mg, 13 %). ^{1}H NMR (600 MHz, $CDCl_3$) 7.3-6.1 (m, 25H), 3.3-3.1 (br s, 2H), 2.4-2.3 (m, 6H), 2.2-2.0 (m, 2H), 1.9-1.0 (m, 28H), 0.8-0.2 (br s, 3H); GPC M_n= 22.1 kg mol^{-1}, M_w= 46.9 kg mol^{-1}, PDI = 2.12.



Polymerization of 11: Following the general procedure outlined above, **11** (314 mg, 0.702 mmol), styrene (220 mg, 2.11 mmol), AIBN (3 mg, 0.0183 mmol), and chlorobenzene (2.0 mL) were combined and reacted. The reaction mixture was cooled, precipitated into 125 mL MeOH and purified by preparatory GPC with $CHCl_3$ as an eluent, concentrated and precipitated into 40 mL MeOH to recover the desired polymer as a white powder (288 mg, 54%). ^{1}H NMR (600 MHz, $CDCl_3$) 7.3-6.1 (m, 36H), 3.6-3.4 (br s, 4 H), 3.4-3.2 (br s, 2 H), 2.4-2.2 (br s, 4 H), 2.0-1.0 (m, 28 H), 0.6 (br s, 3H); GPC M_n= 8.5 kg mol^{-1}, M_w= 14.0 kg mol^{-1}, PDI =1.66.



Polymerization of 12: Following the general procedure outlined above, **12** (200 mg, 0.563 mmol), AIBN (2 mg, 0.0121 mmol), and DMF (1.50 mL) were combined and reacted. The reaction mixture was cooled and precipitated into 100 mL of cold Et_2O to recover the desired polymer as a white powder (140 mg, 70 %). ^{1}H NMR (600 MHz, $CDCl_3$) 7.7-7.4 (m, 1H), 6.9-6.1 (m, 4H), 5.5-5.2 (m, 2H), 3.6-3.4 (m, 2H), 2.0-1.0 (m, 12H); IR (ATR) 3155, 3004, 2945, 2856, 1779, 1736, 1515, 1456, 1427, 1382, 1320, 1276, 1204, 1050, 983, 965, 726 cm^{-1}; GPC M_n= 44.9 kg mol^{-1}, M_w= 87.8 kg mol^{-1}, PDI=1.95; DSC: T_g = 135.3 °C.

Additional Characterization

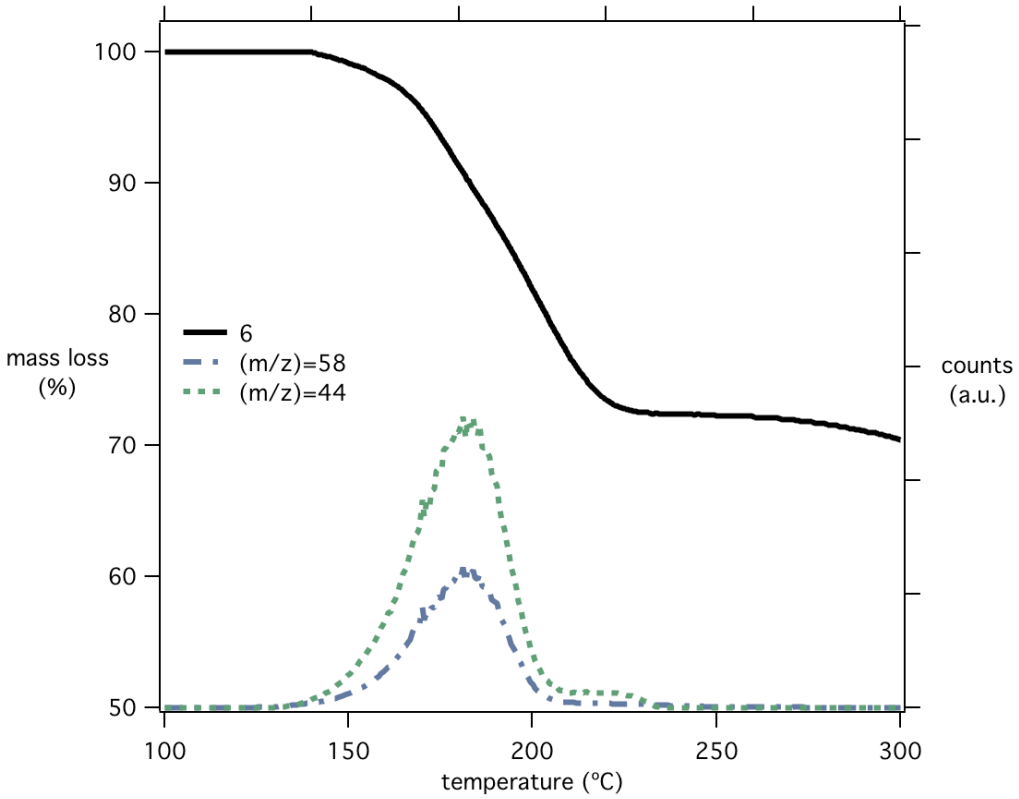


Figure S1: TGA coupled mass spectroscopy for polymer **6** showing the coincident loss of acetone and CO_2 upon thermolysis.

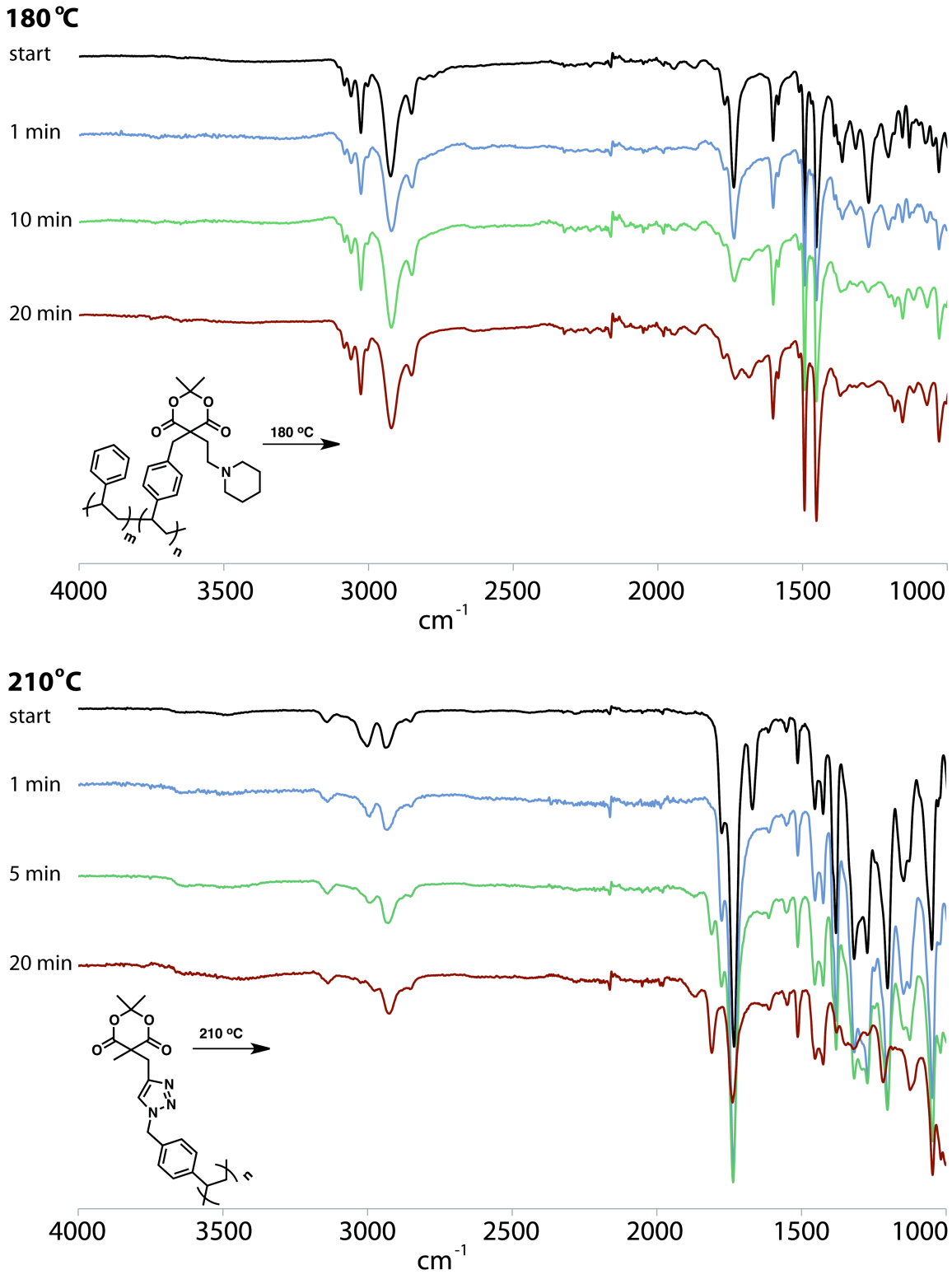


Figure S2: IR plots of polymers at various points during thermolysis. All materials were highly insoluble (crosslinked), but no stable ketene is observed at ~2100 cm^{-1}. The evolution of the carbonyl region is visible in both samples.

Additional Computational Figures

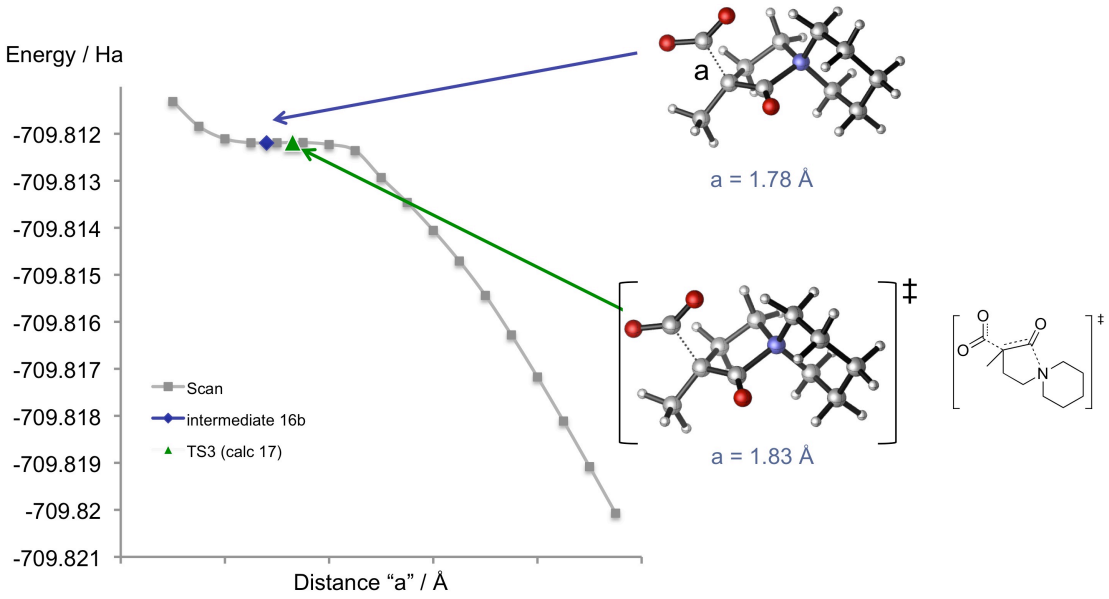


Figure S3: Intrinsic reaction coordinate scan for the decarboxylation of intermediate **14**. The scan shows the absence of an energy minimum for the transition, indicating the favorable loss of CO_2 from the calculated transition structure.

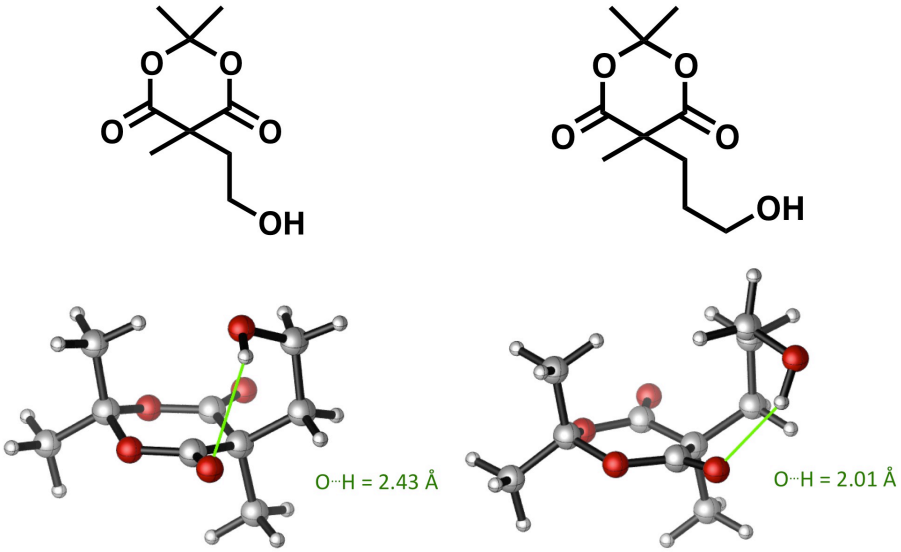


Figure S4: Calculated minimum energy structures for molecules **16** and **17**. The short hydrogen bonding distance of molecules **17** is facilitated by the three carbon spacer attaching the alcohol to the Meldrum's acid ring.

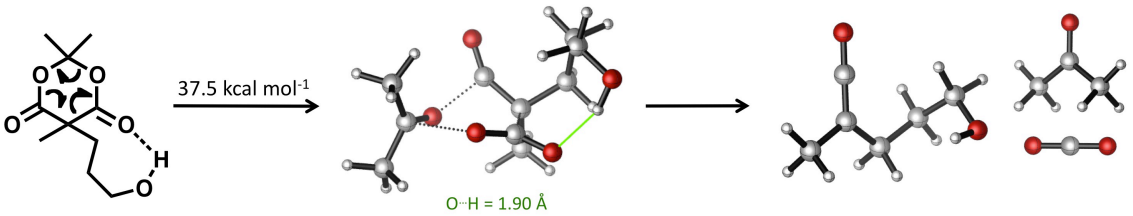


Figure S5: The calculated transition structure for molecule **17** shows the importance of the hydrogen bond interacting with the carbonyl of the CO_2 fragment during thermolysis.

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