Supporting Information

Effect of Polymer Crosslinks on Oxygen Diffusion in Glassy PMMA Films

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General Synthetic Procedures and the Synthesis of Individual Compounds

Commercially available starting materials were used without further purification. THF was freshly distilled over sodium wire. CH_2Cl_2 and triethylamine were distilled over CaH₂. Flash chromatography was performed using Merck silica gel 60 (230-400 mesh). The ¹H and ¹³C NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer at 400 and 100 MHz respectively. Chemical shifts are reported with the solvent as the reference (¹H: CDCl₃: δ 7.26 ppm, d₆-DMSO: δ 2.50 ppm, ¹³C: CDCl₃ δ 77.0 ppm, d₆-DMSO: δ 39.5). MALDI TOF measurements were performed using a Bruker Autoflex spectrometer. Melting points were taken on a Stuart Scientific capillary melting point apparatus and are uncorrected. HRMS was done on a Micromass LCT ES-TOF spectrometer. Yields refer to spectroscopically pure materials.

The numbers used to denote the respective compounds are also shown in Scheme 1 of the manuscript.

2,4-Bis-(4-hydroxyphenyl)cyclobutane-1,3-dicarboxylic acid (2)¹

In a cylindrical glass cell, with a quartz entrance-window, microcrystalline coumaric acid (1) (5.5 g, 33.5 mmol) was suspended in H₂O (100 mL) and exposed to an *Ushio* 200 W Xe(Hg) lamp for 6 days. The lamp output was filtered through a 3 cm water filter, a 1 mm *Pyrex* filter and a 1mm *Schott* UG11 filter to remove light below 250 nm and above 400 nm. After irradiation, and upon filtration and 3 h Soxhlet extraction with ether, we obtained 5.16 g (15.7 mmol, 94 %) of **2**: mp 344 °C dec. (lit. mp 335°C dec.)¹; ¹H NMR (DMSO-*d*₆, 400 MHz) δ 3.64 (dd, 2H, J_{a,a} = 7.4 Hz, J_{a,e} = 10.3 Hz), 4.12 (dd, 2H, J_{a,a} = 7.4 Hz, J_{a,e} = 10.3 Hz), 6.69 (d, 4H, J = 8.4 Hz), 7.12 (d, 4H, J = 8.4 Hz), 9.28 (s, 2H), 11.99 (s, 2H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 40.2, 46.7, 114.9, 128.7, 129.6, 156.1, 173.1.

Due to the orientation imposed by the crystal structure of $\mathbf{1}$, only one stereoisomer of $\mathbf{2}$ is formed.² Moreover, due to the orientation imposed by its crystal structure, it is not possible to irradiate 4-methoxy cinnamic acid in its solid state to directly obtain the cyclic product $\mathbf{4}$.²

2,4-Bis-(4-methoxyphenyl)cyclobutane-1,3-dicarboxylic acid dimethyl ester (3)

A 100 mL one-neck round-bottom flask was charged with **2** (2.0 g, 6.09 mmol) and dissolved in aqueous NaOH (2M, 12.5 mL). The flask was sealed and the reddish-brown solution was purged with nitrogen via a syringe. Dimethyl sulfate (2.3 mL, 24.1 mmol) was added dropwise via a syringe and the reaction flask was heated up to 50°C. After 90 min. of stirring, NaOH (7.5 M, 0.4 mL) and dimethyl sulfate (0.28 mL, 2.93 mmol) were added dropwise via a syringe. This was repeated two more times in 30 min. intervals. The resulting suspension was filtered and the solid was dissolved in CH₂Cl₂, dried over MgSO₄, and concentrated. Flash chromatography on silica gel (pentane/EtOAc = 60/40, v/v) gave 2.14 g (5.57 mmol, 91 %) of **3**: mp 130-132 °C; ¹H NMR (CDCl₃, 400 MHz) δ 3.33 (s, 6H), 3.79 (s, 6H), 3.90 (dd, 2H, J_{a,a} = 7.2 Hz, J_{a,e} = 10.6 Hz), 4.38 (dd, 2H, J_{a,a} = 7.3 Hz, J_{a,e} = 10.5 Hz), 6.86 (d, 4H, J = 8.7 Hz), 7.21 (d, 4H, J = 8.7 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 40.7, 47.0, 51.5, 55.2, 113.7, 128.5, 130.7, 158.6, 172.5; HRMS (ES) *m/z* calcd for [C₂₂H₂₄O₆ + Na]⁺ 407.1471, found 407.1472.

2,4-Bis-(4-methoxyphenyl)cyclobutane-1,3-dicarboxylic acid (4)

A 100 mL round-bottom flask was charged with **3** (0.60 g, 1.56 mmol), THF (20 mL), H_2O (6.8 mL), MeOH (6.8 mL), and LiOH (150 mg, 6.26 mmol). The solution was stirred at rt for 18 h. The solvents were removed under reduced pressure, and the resultant solid was dissolved in H_2O , washed with CH_2Cl_2 , acidified with HCl (2M), and filtered to give 0.55 g of **4**

(1.54 mmol, 96 %): mp 256-258 °C (lit. mp 260-261 °C)¹; ¹H NMR (DMSO-*d*₆, 400 MHz)) δ 3.73 (m, 8H), 4.21 (dd, 2H, J_{a,a} = 7.5 Hz, J_{a,e} = 10.1 Hz), 6.88 (d, 4H, J = 8.6 Hz), 7.27 (d, 4H, J = 8.6 Hz), 12.04 (br, 2H); ¹³C NMR (DMSO-d₆, 100 MHz) δ 40.2, 46.5, 55.0, 113.5, 128.7, 131.3, 158.0, 173.0; HRMS (ES) *m/z* calcd for [C₂₀H₂₀O₆ + Na]⁺ 379.1158, found 379.1145.

During the basic hydrolysis, the α -carbon can be reversibly deprotonated leading to epimerization and formation of ~ 15 % of different diastereoisomers. This can be seen from, for example, the ¹H NMR (DMSO-d₆, 400 MHz) δ 4.10 (t, 0.17 H, J = 9.9 Hz), 4.31 (t, 0.22 H, J = 10.9 Hz) for one of the cyclobutane hydrogen atoms (δ 4.21 (dd, 2H, J_{a,a} = 7.5 Hz, J_{a,e} = 10.1 Hz)).

2,4-Bis-(4-methoxyphenyl)cyclobutane-1,3-dicarbonyl dichloride (5)

A 50 mL round-bottom flask was charged with **4** (0.30 g, 0.84 mmol) and CH₂Cl₂ (18 mL). The flask was cooled to 0 °C and oxalylchloride (0.30 mL, 3.44 mmol) and 1 drop of DMF were added under a slow stream of nitrogen. The mixture was warmed to rt and stirred for 2h under a slow stream of nitrogen. Unreacted oxalylchloride and CH₂Cl₂ were removed under reduced pressure and left behind 0.32 g of **5** (0.82 mmol, 97 %): mp 147-148 °C (lit. mp 145-147 °C)¹; ¹H NMR (CDCl₃, 400 MHz) δ 3.75 (s, 6H), 4.21 (dd, 2H, J_{a,a} = 7.1 Hz , J_{a,e} = 10.8 Hz), 4.50 (dd, 2H, J_{a,a} = 7.3 Hz , J_{a,e} = 10.8 Hz), 6.85 (d, 4H, J = 8.7), 7.17 (d, 4H, J = 8.7); ¹³C NMR (CDCl₃, 100 MHz) δ 43.4, 55.3, 57.8, 114.3, 127.6, 128.9, 159.4, 173.5.

2,4-Bis-(4-methoxyphenyl)cyclobutane-1,3-dicarboxylic acid bis-[2-(2-methyl-acryloyloxy)ethyl] ester (6)

A 50 mL round-bottom flask was charged with **5** (0.30 g, 0.76 mmol), dichloromethane (20 mL), triethylamine (0.32 mL, 2.30 mmol), and *N*,*N*-dimethyl-4-aminopyridine (DMAP) (5.0 mg, 0.04 mmol), sealed, and purged with nitrogen. Hereafter, 2-hydroxyethyl methacrylate (HEMA) (0.27 mL, 3.10 mmol) was added dropwise via a syringe. The mixture was stirred at rt for 3 h, washed with saturated aqueous NH₄Cl, and dried over MgSO₄. Flash chromatography on silica gel (pentane/EtOAc = 50:50, v/v) gave 0.27 g of **6** (0.47 mmol, 61 %): yellow oil; ¹H NMR (CDCl₃, 400 MHz) δ 1.91 (s, 6H), 3.77 (s, 6 H), 3.9 (m, 10 H), 4.39 (dd, 2 H, J_{a,a} = 7.3 Hz, J_{a,e} = 10.5 Hz), 5.57 (s, 2 H), 6.06 (s, 2H), 6.82 (d, 4 H, J = 8.7 Hz), 7.20 (d, 4 H, J = 8.7 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 18.2, 40.5, 46.9, 55.1, 62.0, 62.2, 113.6, 125.9, 128.5, 130.3, 135.8, 158.6, 166.8, 171.6; MS (MALDI TOF) *m/z* calcd for [C₃₂H₃₆O₁₀ + Na]⁺ 603.6, found 603.5.

Poly(methyl methacrylate-co-6)

methacrylate was received from Sigma Aldrich Methyl and the inhibitor was chromatographically removed using a pre-packed column designed for this purpose (Sigma Aldrich). Subsequently, the monomer was distilled over CaH₂. 2,2'-Azobis(isobutyronitrile) (AIBN), used as the free-radical initiator, was first recrystallized from methanol and dried to Toluene was freshly distilled. Glass-ampoules were filled with methyl constant weight. methacrylate (9.00 mL, 84.5 mmol), 5 mol% AIBN (694 mg, 4.22 mmol), toluene (13.5 mL) and, depending on the desired extent of crosslinking in the sample, 0 to 2.0 mol% of 6. Hereafter, the sample was de-oxygenated with three freeze-pump-thaw cycles. The ampoules were then sealed and placed in an oil-bath at 60 °C for 3 h, after which they were immersed in liquid nitrogen. After equilibration to room temperature, the ampoules were broken and the liquid reaction mixture poured into a tenfold excess of methanol. The resulting polymer was filtered off and dried overnight at 50 °C under vacuum.

NMR Spectra



Figure S1. ¹H and ¹³C NMR spectra of **2**.



Figure S2. ¹H and ¹³C NMR spectra of **3**.



Figure S3. ¹H and ¹³C NMR spectra of **4**.



Figure S4. ¹H and ¹³C NMR spectra of 5.





Figure S5. ¹H and ¹³C NMR spectra of 6.

Crystal Structure of 2,4-Bis(4-methoxy-phenyl)-cyclobutane-1,3-dicarboxylic acid (4)

A small amount of **4** was recrystallized (acetic acid/EtOAc = 50/50, v/v) and used for the determination of the crystal structure. Single crystal diffraction data were acquired for 24 h using a Bruker ApexII CCD diffractometer.



Figure S6. ORTEP drawing of the asymmetric unit.

Crystal data for 4: C₂₀H₂₀O₆, M = 356.36, triclinic, Space group P -1 (no. 2), a = 5.4015(4) Å, b = 8.1001(6) Å, c = 10.5161(7) Å, a = 89.601(5) °, $\beta = 84.818(5)$ °, $\gamma = 72.954(4)$ °, V = 438.01(6) Å³, T = 100 K, Z = 1, D_c = 1.351 g cm⁻³, μ (Mo K α , $\lambda = 0.7107$ Å) = 0.1 mm⁻¹, 6979 reflections collected, 2383 unique [$R_{int} = 0.0413$], which were used in all calculations. Refinement on F², final R(F) = 0.0912, R_w(F2) = 0.1263.

Molecular formula $C_{20}H_{20}O_6$ Formula weight 356.36 Crystal system Triclinic Space Group P -1 Z 1 a, Å 5.4015 b, Å 8.1001 c, Å 10.5161 a, ° 89.601 β , ° 72.954 γ , Å ³ 438.01 ρ , g/cm ³ 1.351 Type of radiation Mo K _a μ , mm ⁻¹ 0.1 T, K 100 R _{int} 0.0413 Number of measured reflections 6979 Number of parameters 120 R(F ²), all refl 0.0912 R _w (F ²), used refl 0.1263 Goodness of fit 1.021		
Formula weight 356.36 Crystal system Triclinic Space Group $P - 1$ Z 1 a, Å 5.4015 b, Å 8.1001 c, Å 10.5161 a, ° 89.601 β , ° 72.954 γ , ° 72.954 γ , Å ³ 438.01 ρ , g/cm ³ 1.351 Type of radiation Mo K _a μ , mm ⁻¹ 0.1 T, K 100 R _{int} 0.0413 Number of measured reflections 6979 Number of parameters 120 R(F ²), used refl 0.0912 R _w (F ²), used refl 0.1263 Goodness of fit 1.021	Molecular formula	$C_{20}H_{20}O_6$
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Space Group P -1 Z 1 $a, Å$ 5.4015 $b, Å$ 8.1001 $c, Å$ 10.5161 $a, °$ 89.601 $\beta, °$ 84.818 $\gamma, °$ 72.954 $V, Å^3$ 438.01 $\rho, g/cm^3$ 1.351 Type of radiation Mo K _a μ, mm^{-1} 0.1 T, K 100 Rint 0.0413 Number of measured reflections 6979 Number of parameters 120 R(F ²), used refl 0.1263 Goodness of fit 1.021	Crystal system	Triclinic
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Goodness of fit 1.021	$R_w(F^2)$, used refl	0.1263
	Goodness of fit	1.021

 Table S1. Crystallographic data for 4.

UV-VIS Spectra of T(3-HOP)P

In previous studies of porphyrins dissolved in PMMA, we have occasionally observed what appear to be reversible solvent-dependent spectral shifts. In the present study, we decided to investigate this phenomenon further.

The porphyrin T(3-HOP)P and commercial grade PMMA were dissolved in butanone. Samples were prepared using PMMA with 6 different molecular weights ranging from 15,000 to 540,000 g mol⁻¹ (Scientific Polymer Products and Sigma Aldrich). The respective solutions were spin-coated onto glass substrates and absorption spectra were recorded as a function of time (Figure S7).



Figure S7. UV-VIS absorption spectra of T(3-HOP)P in a 10 μ m thick PMMA film, M_w of 15,000 g mol⁻¹. The spectra were recorded as a function of time over a period of 4 days. With the exception of the incident light from the diode array spectrometer, and occasional and minimal exposure to ambient room lighting, the samples were not irradiated.

As illustrated in Figure S7, the absorption profile of T(3-HOP)P dissolved in 15,000 g mol⁻¹ PMMA clearly changes over time. This rate of change decreases when higher molecular weight PMMA is used. The presence of the isosbestic point at 430 nm suggests an equilibrium between two distinct species. In all cases, the original position of the Soret band at 420 nm was restored when the PMMA films containing T(3-HOP)P were dissolved in THF indicating the reversibility of this process.

These data are consistent with a mobility-dependent process of either porphyrin aggregation or of complex formation with an additive in the polymer (*i.e.*, dye diffusion is less facile in the higher molecular weight PMMA samples). It is interesting to note that, in preliminary experiments, it appears that exposure of the dye-containing film to light may increase the rate at which the spectral changes are observed. This could reflect the effects of local heating in the polymer that result from non-radiative deactivation of the porphyrin.

As noted in the Experimental Section of the manuscript, all of our oxygen diffusion experiments were performed using samples in which there was no evidence of this apparent aggregation/complexation of the singlet oxygen sensitizer. Indeed, the phenomenon described herein was only observed in commercially available polymers, not in the polymers prepared for our crosslink study.

References

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