

Supporting Information

In-cage and out-of-cage combinations of benzylic radical pairs in the glassy and melted states of poly(alkyl methacrylate)s

Shibu Abraham,^a Indrajit Ghosh,^b Werner M. Nau,^b Carlos Chesta,^c Steven J. Pas,^{d,e} Anita J. Hill,^{d,e} and Richard G. Weiss^{a,*}

^aDepartment of Chemistry, Georgetown University, Washington DC 20057-1227, ^bSchool of Engineering and Science, Jacobs University Bremen, Campus Ring 1, D-28759 Bremen, Germany, ^cDepartamento de Química, Universidad Nacional de Río Cuarto, 5800-Río Cuarto, Argentina, ^dCSIRO Materials Science and Engineering, Private Bag 33, South Clayton, VIC 3168, Australia, ^eMonash University Department of Materials Engineering, Wellington Road, Clayton, VIC 3800, Australia.

E-mail:weissr@georgetown.edu

1.1. Materials

Cyclohexane (Fischer, 99.9%), hexane (Fischer, HPLC grade), toluene (EMD, 99.5%), ditolylmethane (Pfaltz and Bauer, 95%), and methanol (Fisher, HPLC grade) were used as received. Approximate molecular weights of poly(alkyl methacrylate)s (PAMAs) from information by suppliers (mentioned in main text) are: PEMA-350,000, PCHMA-65,000, PIBMA-70,000, PBMA-180,000, and PHDMA-200,000.

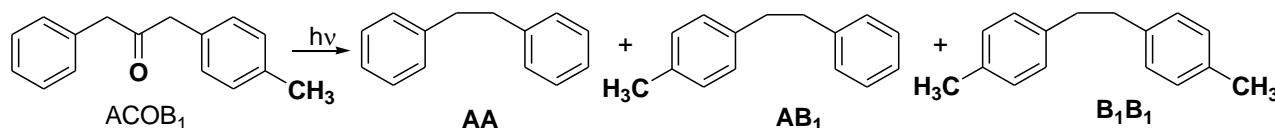
1.2. General procedures for purification of PAMAs

A 10 g aliquot of PBMA, PCHMA or PIBMA was dissolved in 45 mL of warm cyclohexane. After cooling, the solution was poured into 200 mL of stirred methanol. The precipitate was separated by decanting the solution and the white solid was washed with 50 mL of methanol. This procedure was repeated two more times. The precipitate was left under dynamic vacuum (250 mm of Hg) at 333 K for 6 h to remove residual solvent. A 10 g aliquot of PEMA was warmed in 40 mL CH₂Cl₂ until it dissolved. At room temperature, 100 mL of hexane were added and a white precipitate was obtained. The precipitate was washed with 50 mL hexane and separated by decanting the liquid. This procedure was repeated two more times. The solid was dried as described above. A 7.6 g portion of a solution of 30 % PHDMA in toluene was poured into 20 mL of hexane. This mixture was concentrated by evaporation under nitrogen. The polymer was dissolved in 20 mL toluene and precipitated by adding 200 mL methanol. The liquid was decanted from the white solid. This process was repeated twice more and the PHDMA was dried as described above.

1. 3. Analyses

1. 3. 1. Instrument response factors

The photoproducts found after irradiation of 1-(4-methylphenyl)-3-phenyl-2-propanone [ACOB₁] AA, AB₁ and B₁B₁, are shown in Scheme S1.



Scheme S1.

The ratios of [AA]:[AB₁]:[B₁B₁] photoproduct areas under the GC peaks in chromatograms were measured after different periods of irradiation (and % conversions) of ACOB₁ in low viscosity liquid solvents. Assuming that the true ratios are 1:2:1, appropriate multiplication factors for each peak were determined. These instrumental response factors were then used to convert relative peak areas for products from irradiations of ACOB₁ in polymer films into product ratios.

The percentage conversions were calculated using eq S1 after converting the peak areas into relative molar concentrations with the response factors.

$$\text{percent conversion} = 100 \times \frac{[AA] + [AB_1] + [B_1B_1]}{[AB_1] + [AA] + [B_1B_1] + [ACOB_1]} \quad (\text{S1})$$

The instrumental responses obtained for photoproducts on irradiation of a solution of ACOB₁ in the presence of an internal standard were used to determine the correction factor for the starting material, ACOB₁. In this experiment dodecane was used as the internal standard and the percentage conversions were determined using eq S2:

$$\text{percent conversion} = \frac{\left\{ \frac{(A_{ACOB_1})_{t=0}}{(A_{\text{dodecane}})} \right\} - \left\{ \frac{(A_{ACOB_1})_{t=t}}{(A_{\text{dodecane}})} \right\} \times 100}{\left\{ \frac{(A_{ACOB_1})_{t=0}}{(A_{\text{dodecane}})} \right\}} \quad (\text{S2})$$

where $(A_{ACOB_1})_{t=t}$ is the peak area of [ACOB₁] at any irradiation time t , $(A_{ACOB_1})_{t=0}$ is the peak area of [ACOB₁] before irradiation at time $t = 0$, and A_{dodecane} is the peak area of the internal standard, dodecane. Implicit in the use of both eq S1 and eq S2 is the assumption that all of the photoproducts from ACOB₁ are represented by AA, AB₁, and B₁B₁. As mentioned in the main text, this assumption appears to be valid because none of the reasonably expected side products were detected in the GC analyses and the mass balances from the polymers were >90%.

1. 3. 2. Error Analyses

Chromatograms from 3-5 injections of each irradiated sample were averaged and the error limits in F_c values were calculated by standard propagation of error analytical procedures² that led to eq S3.

$$\delta F_c = \frac{2}{([AA] + [AB_1] + [B_1B_1])^2} \sqrt{(([AA] + [B_1B_1]) \delta [AB_1])^2 + ([AB_1] \delta [AA])^2 + ([AB_1] \delta [B_1B_1])^2} \quad (S3)$$

δAA , δAB_1 , and δB_1B_1 are errors in the measurements of products AA, AB_1 and B_1B_1 based on standard deviations of average peak areas. δAA is assumed to be zero in the present study, because the areas of the AB and BB peaks were normalized to the area of the AA peak in each chromatogram.

1.4 Relative quantum yield measurements in a photochemical reactor

ACOB₁, in ethyl acetate (13-18 mM) and in PHDMA and PCHMA (36-40 mol/kg polymer) films, was irradiated at 300 nm through pyrex filters simultaneously at room temperature in a Rayonet merry-go-round (RMA-400) photochemical reactor. Prior to irradiation, the samples were purged with nitrogen gas for 10 min. The windows of the samples were masked with black tape so that the same areas were exposed in each. The initial and final optical densities of the samples at 300 nm were >2 in order to ensure that all of the radiation was absorbed by the ACOB₁; the AA, AB_1 , and B_1B_1 photoproducts have almost no absorbance at 300 nm. During the 30 min irradiation period, the approximate conversions were assessed by UV-vis absorption measurements. The products and remaining ACOB₁ were extracted exhaustively from the PHDMA and PCHMA films with ethyl acetate. Conversions were calculated from knowledge of the initial concentrations before and after irradiation. The latter was calculated using UV-vis absorption spectra and extinction coefficients of ACOB₁ in ethyl acetate. Thus, 51 % conversion in ethyl acetate and 12 % conversion in PHDMA were found in one run and 33 % conversion in ethyl acetate and 10 % in PCHMA were observed in another.

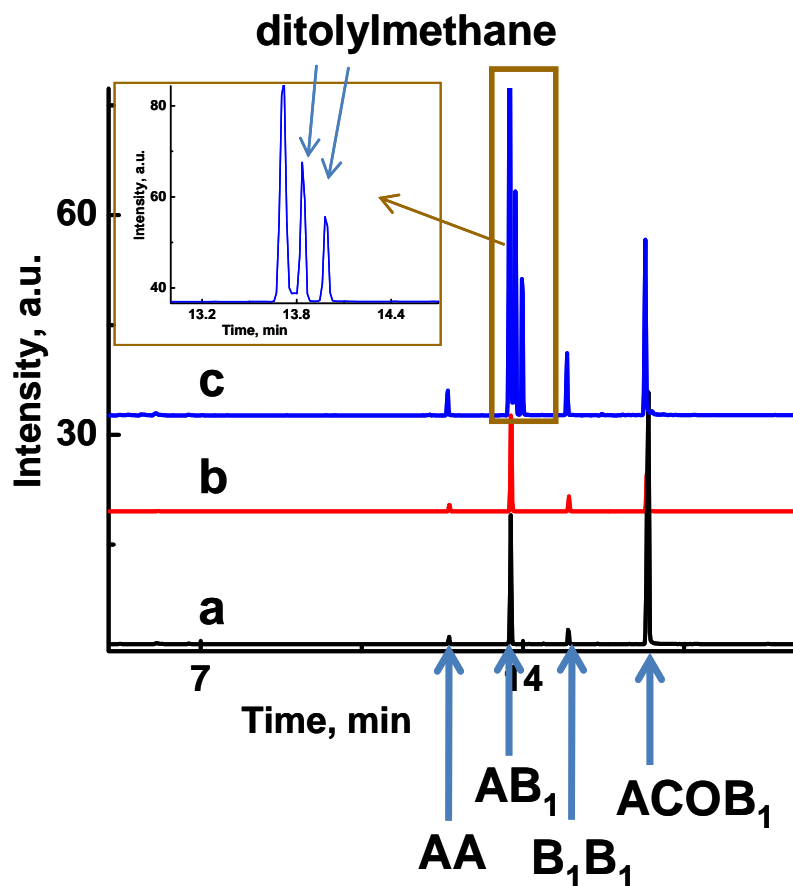


Figure S1. GC chromatogram of ACOB₁ and photoproducts extracted from PBMA after irradiations for different intervals of time: (a) 17 % conversion; (b) 62 % conversion; (c) 62 % conversion, co-injected with the isomers of ditolylmethane (the cross-coupled Fischer photoproducts, analogous to AB₁, and expected from in-cage combination of A·/B₁· pairs³); the more probable cross-coupled Fischer photoproduct expected from combination of pairs of cage-escaped A· radicals, is phenyltolylmethane. The expanded region shows the peaks for AB₁ and the two isomers of the expected Fischer photoproducts.

1. 5. Transient absorption studies

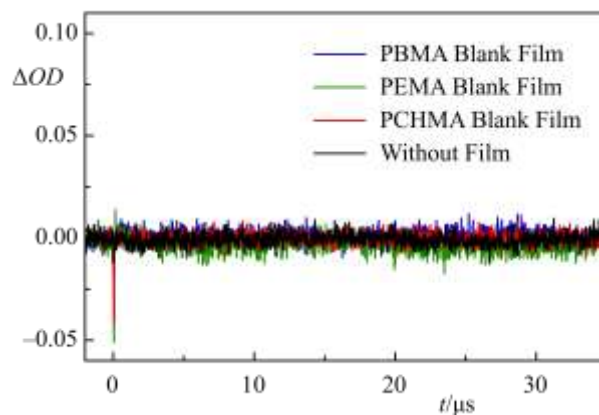


Figure S2. Response of the photomultiplier of the laser flash set-up without film and with undoped polymer films, monitored at 320 nm. The emission spike at $t = 0$ corresponds to scattered 308 nm laser light caused by the blank films.

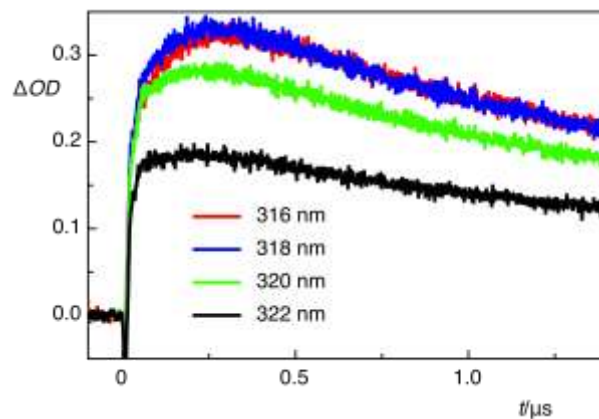


Figure S3. Transient absorption rises and decays of benzylic radicals produced upon laser flash photolysis of ACOB₁ in *n*-hexane at 298 K monitored at different wavelengths. Note the time-resolved growth in transient absorption at short times (< 500 ns).

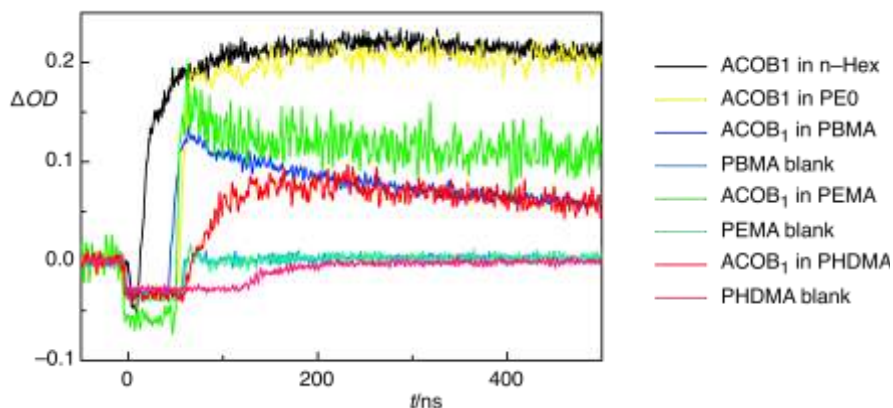


Figure S4. Short-time scale transient absorption decays monitored at 320 nm of benzylic radicals produced upon laser flash photolysis of ACOB₁ in different PAMA films at 298 K and in *n*-hexane and a completely amorphous PE film, PE0; also shown for comparison is the response of the apparatus to scattered light from the undoped PAMA films. Segments of the traces with negative ΔOD correspond to scattered light, the interference of which is very small for *n*-hexane solution, and very strong for PHDMA films. Note that a time-resolved rise is observed, subsequent to the scattered light response, for ACOB₁ in *n*-hexane solution and PE0 films. This rise is absent for the PBMA and PEMA films, where an immediate decay is observed. For ACOB₁ in PHDMA films, the very strong scattering profile prevents the assignment of a time-resolved rise as being due to a transient absorption phenomenon.

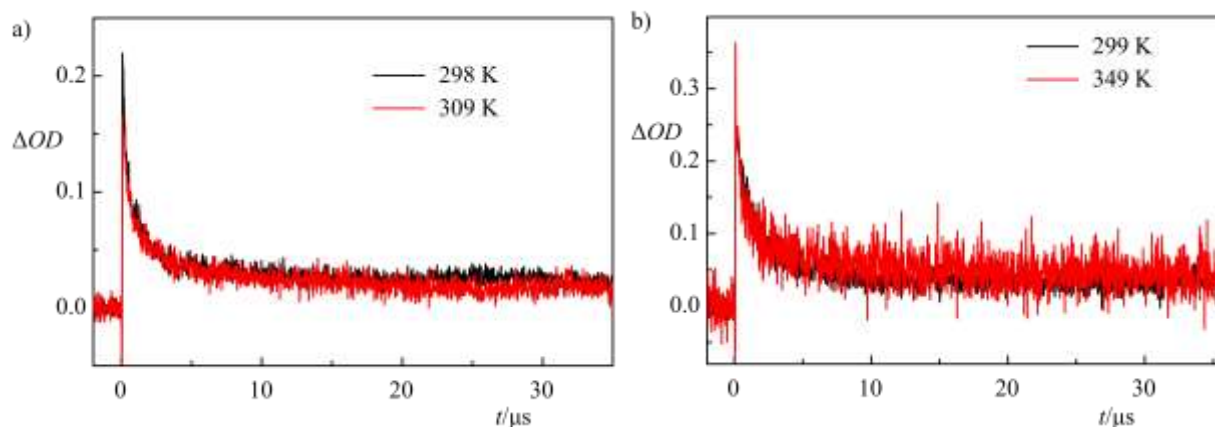


Figure S5. Transient absorption decay traces monitored at 320 nm of benzylic radicals produced by laser flash photolysis of ACOB₁ in (a) PBMA and (b) PEMA polymer films at ambient (black) and elevated (red) temperatures.

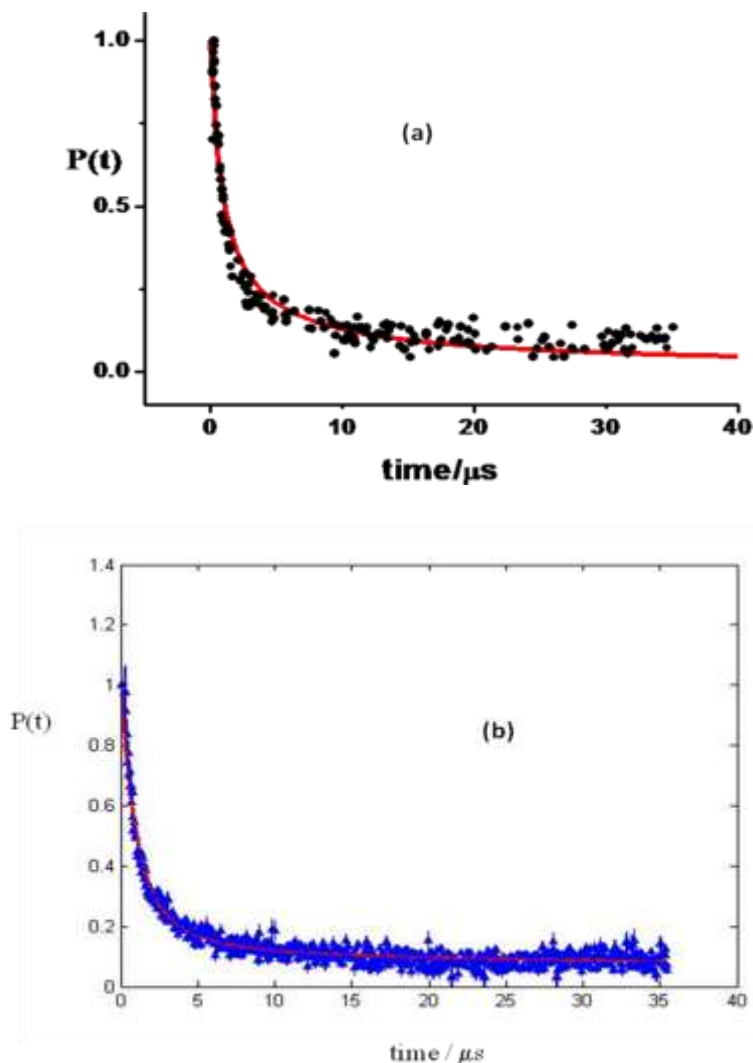


Figure S6. (a) Decay of benzylic radicals in PHDMA (●) at 308 K and the fitted trace (red line) according to the Kutsenova model (eq 3) in the main text. Note the deviation of the best fit from the data points at $t > 20 \mu\text{s}$; (b) Decay of benzylic radicals in PHDMA (blue ▲) at 308 K and the fitted trace (red line) according to Khudyakov model (eq 4) in the main text.

1. 6. Positronium annihilation lifetime measurements

Table S1. Effect of temperature on *o*-positronium (*o*-Ps) intensities and lifetimes in PEMA, as well as calculated free volumes.

T [K]	<i>o</i> -Ps Intensity [%]	SD ^a [%]	<i>o</i> -Ps Lifetime [ns]	SD ^a [ns]	Radius [Å]	SD ^a [Å]	Volume [Å ³]	SD ^a [Å ³]
296	25.54	0.43	2.161	0.022	2.996	0.018	112.7	2.1

306	25.59	0.27	2.204	0.010	3.033	0.009	116.9	1.0
311	25.99	0.22	2.206	0.015	3.035	0.013	117.1	1.5
316	25.80	0.43	2.230	0.022	3.056	0.018	119.5	2.2
321	26.14	0.24	2.242	0.013	3.066	0.011	120.7	1.3
326	27.29	0.18	2.237	0.010	3.061	0.009	120.1	1.0
331	27.67	0.18	2.252	0.006	3.074	0.005	121.6	0.6
336	29.29	0.13	2.228	0.006	3.054	0.005	119.3	0.6
341	28.96	0.41	2.301	0.027	3.115	0.022	126.6	2.7
346	29.92	0.39	2.306	0.027	3.119	0.022	127.1	2.7
351	30.50	0.16	2.339	0.013	3.146	0.010	130.4	1.3
356	31.52	0.10	2.349	0.001	3.154	0.001	131.4	0.2
361	31.69	0.48	2.416	0.018	3.207	0.014	138.2	1.8
366	32.14	0.32	2.455	0.008	3.238	0.006	142.2	0.8

^a One standard deviation (SD) of a minimum of 3 samples.

Table S2. Effect of temperature on *o*-positronium (*o*-Ps) intensities and lifetimes in PBMA, as well as calculated free volumes. Standard deviations (SD) of measurements are also shown.

<i>T</i> [K]	<i>o</i> -Ps Intensity [%]	SD ^a [%]	<i>o</i> -Ps Lifetime [ns]	SD ^a [ns]	Radius [Å]	SD ^a [Å]	Volume [Å ³]	SD ^a [Å ³]
258	27.69	1.64	2.199	0.056	3.029	0.047	116.4	5.5
263	28.03	0.66	2.214	0.030	3.042	0.025	117.9	3.0
268	28.45	0.50	2.254	0.028	3.075	0.023	121.8	2.8
273	28.55	0.71	2.279	0.026	3.096	0.021	124.3	2.6
278	28.25	0.86	2.321	0.038	3.131	0.031	128.5	3.9
283	28.99	0.49	2.347	0.017	3.152	0.014	131.2	1.7
288	29.53	0.31	2.385	0.024	3.183	0.019	135.1	2.4

293	29.37	1.39	2.415	0.051	3.207	0.040	138.1	5.3
298	30.19	0.32	2.452	0.023	3.236	0.018	141.9	2.4
298	29.95	0.45	2.454	0.027	3.237	0.021	142.1	2.8
303	30.04	0.37	2.483	0.022	3.260	0.017	145.1	2.2
308	30.34	0.28	2.524	0.014	3.291	0.011	149.3	1.5
313	30.36	0.34	2.561	0.023	3.320	0.017	153.3	2.4
318	31.02	0.31	2.574	0.029	3.330	0.022	154.7	3.0

^a One standard deviation (SD) of a minimum of 3 samples.

Table S3. Effect of temperature on *o*-positronium (*o*-Ps) intensities and lifetime in PIBMA, as well as calculated free volumes. Standard deviations (SD) of measurements are also shown.

<i>T</i> [K]	<i>o</i>-Ps Intensity [%]	SD^a [%]	<i>o</i>-Ps Lifetime [ns]	SD [ns]	Radius [Å]	SD [Å]	Volume [Å³]	SD [Å³]
296	29.30	0.21	2.548	0.017	3.310	0.013	151.9	1.8
301	28.87	0.71	2.628	0.042	3.370	0.031	160.3	4.5
306	28.71	0.29	2.703	0.018	3.426	0.013	168.4	1.9
311	29.22	0.79	2.730	0.035	3.445	0.026	171.2	3.8
316	29.06	0.43	2.781	0.024	3.482	0.017	176.8	2.6
321	29.59	0.29	2.811	0.027	3.503	0.019	180.1	2.9
326	30.62	0.73	2.896	0.046	3.563	0.031	189.5	5.1
331	31.12	0.24	2.923	0.016	3.581	0.011	192.4	1.8
336	30.83	0.24	3.002	0.019	3.635	0.012	201.2	2.1
341	30.62	0.78	3.027	0.047	3.652	0.031	204.0	5.2
346	30.29	0.40	3.036	0.031	3.658	0.020	205.0	3.4
351	30.11	0.65	3.055	0.056	3.671	0.038	207.2	6.4
356	29.00	0.24	3.105	0.009	3.704	0.006	212.9	1.0

^a One standard deviation (SD) of a minimum of 3 samples.

Table S4. Effect of temperature on *o*-positronium (*o*-Ps) intensities and lifetime in PCHMA, as well as calculated free volumes. Standard deviations (SD) of measurements are also shown.

<i>T</i> [K]	<i>o</i> -Ps Intensity [%]	SD ^a [%]	<i>o</i> -Ps Lifetime [ns]	SD ^a [ns]	Radius [Å]	SD ^a [Å]	Volume [Å ³]	SD ^a [Å ³]
347	23.58	1.03	2.232	0.043	3.057	0.036	119.6	4.3
352	25.04	0.27	2.220	0.012	3.047	0.009	118.5	1.1
357	25.99	0.36	2.244	0.023	3.067	0.019	120.9	2.3
362	26.59	0.48	2.262	0.034	3.083	0.028	122.7	3.3
367	27.32	0.47	2.304	0.028	3.117	0.023	126.8	2.9
372	29.12	0.47	2.290	0.028	3.105	0.023	125.4	2.8
377	28.84	0.66	2.343	0.029	3.149	0.023	130.8	2.9
382	28.79	0.13	2.371	0.008	3.171	0.006	133.6	0.8
387	28.58	0.40	2.430	0.024	3.218	0.019	139.6	2.5
392	29.17	0.52	2.473	0.022	3.252	0.017	144.1	2.3
397	29.38	0.52	2.535	0.020	3.300	0.016	150.5	2.1
402	30.32	0.27	2.559	0.017	3.318	0.013	153.1	1.8
407	31.05	0.47	2.588	0.027	3.340	0.021	156.1	2.9

^a One standard deviation (SD) of a minimum of 3 samples.

Table S5. Effect of temperature on *o*-positronium (*o*-Ps) intensities and lifetime in PHDMA, as well as calculated free volume. Standard deviations (SD) of measurements are also shown.

<i>T</i> [K]	<i>o</i> -Ps Intensity [%]	SD ^a [%]	<i>o</i> -Ps Lifetime [ns]	SD ^a [ns]	Radius [Å]	SD ^a [Å]	Volume [Å ³]	SD ^a [Å ³]
258	20.17	0.31	2.182	0.035	3.014	0.030	114.7	3.4
263	20.46	0.29	2.230	0.025	3.055	0.021	119.4	2.5

268	20.34	0.21	2.286	0.016	3.102	0.013	125.0	1.6
273	20.76	0.05	2.327	0.011	3.136	0.009	129.1	1.1
278	20.64	0.21	2.414	0.010	3.205	0.008	137.9	1.0
283	20.85	0.27	2.481	0.028	3.258	0.022	144.9	2.9
288	21.21	0.49	2.549	0.034	3.311	0.026	152.0	3.6
290	21.92	0.27	2.633	0.027	3.374	0.019	160.8	2.8
292	22.51	0.23	2.673	0.023	3.403	0.017	165.1	2.5
293	23.37	0.12	2.747	0.020	3.457	0.015	173.1	2.2
295	26.15	0.13	2.821	0.018	3.510	0.013	181.2	2.0
296	27.48	0.27	2.836	0.022	3.520	0.015	182.8	2.4
297	27.88	0.21	2.839	0.023	3.523	0.016	183.2	2.5
298	27.88	0.25	2.854	0.017	3.534	0.012	184.8	1.9
303	27.59	0.17	2.879	0.014	3.551	0.010	187.5	1.6
308	27.97	0.48	2.891	0.040	3.559	0.027	188.8	4.4
313	28.24	0.22	2.904	0.023	3.568	0.016	190.3	2.6
318	28.17	0.33	2.906	0.023	3.570	0.016	190.5	2.5

^a One standard deviation (SD) of a minimum of 3 samples.

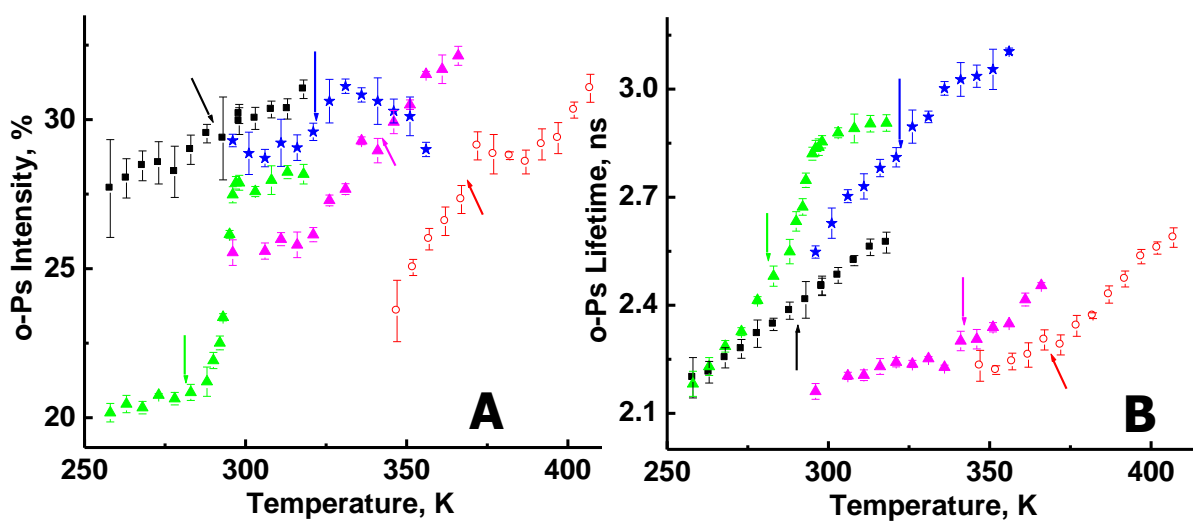


Figure S7. Effect of temperature on (A) *o*-Ps intensities and (B) *o*-Ps lifetimes in PAMAs: PCHMA (○), PEMA (△), PIBMA (★), PBMA (■) and B) PHDMA (▲). Arrows refer to melting (for PHDMA) or glass transition temperatures determined from differential scanning calorimetry thermograms.

1.7. Dependence of F_c on temperature

Table S6. Dependence of product distributions on temperature for irradiations of ACOB₁ in PHDMA films ($T_m = 281$ K).

T [K]	percent conversion ^a	[AA]:[AB ₁]:[B ₁ B ₁]	F_c
258 ± 1	21 ± 2	1.0 : 9.0 ± 0.7 : 1.3 ± 0.1	0.59 ± 0.02
261 ± 2	31 ± 2	1.0 : 10.5 ± 0.2 : 1.4 ± 0.1	0.61 ± 0.02
261 ± 2	20 ± 1	1.0 : 7.1 ± 0.3 : 1.4 ± 0.01	0.50 ± 0.02
261 ± 2	19 ± 2	1.0 : 6.2 ± 0.3 : 1.2 ± 0.1	0.47 ± 0.02
271 ± 1	18 ± 1	1.0 : 12.7 ± 0.2 : 1.5 ± 0.1	0.67 ± 0.01
271 ± 1	17 ± 1	1.0 : 10.9 ± 0.4 : 1.5 ± 0.1	0.63 ± 0.02
274 ± 1	20 ± 2	1.0 : 9.1 ± 0.2 : 1.4 ± 0.1	0.58 ± 0.01
274 ± 1	15 ± 1	1.0 : 8.0 ± 0.1 : 1.4 ± 0.03	0.53 ± 0.02
274 ± 1	31 ± 2	1.0 : 7.3 ± 0.6 : 1.3 ± 0.18	0.52 ± 0.04
296 ± 1	39 ± 2	1.0 : 3.2 ± 0.1 : 1.3 ± 0.1	0.16 ± 0.03
296 ± 1	45 ± 1	1.0 : 2.9 ± 0.02 : 1.1 ± 0.03	0.16 ± 0.01
304 ± 2	43 ± 2	1.0 : 3.0 ± 0.2 : 1.2 ± 0.02	0.17 ± 0.03
304 ± 2	42 ± 4	1.0 : 3.1 ± 0.1 : 1.2 ± 0.07	0.16 ± 0.02
313 ± 1	25 ± 2	1.0 : 3.6 ± 0.1 : 1.3 ± 0.1	0.20 ± 0.02
313 ± 1	37 ± 1	1.0 : 3.0 ± 0.1 : 1.3 ± 0.1	0.13 ± 0.03

^a Percent conversions according to eq S1.

Table S7. Dependence of product distributions on temperature from irradiations of ACOB₁ in PBMA films ($T_g = 290$ K).

T [K]	percent conversion ^a	[AA]:[AB ₁]:[B ₁ B ₁]	F_c
260 ± 2	4 ± 1	1.0 : 10.8 ± 0.2 : 1.3 ± 0.1	0.65 ± 0.01
274 ± 2	4 ± 1	1.0 : 11.7 ± 2.1 : 1.6 ± 0.3	0.63 ± 0.06
274 ± 2	55 ± 2	1.0 : 9.7 ± 0.9 : 1.1 ± 0.2	0.64 ± 0.04
280 ± 1	28 ± 2	1.0 : 18.2 ± 0.9 : 1.6 ± 0.2	0.75 ± 0.02
301 ± 1	18 ± 1	1.0 : 19.3 ± 0.2 : 1.3 ± 0.01	0.79 ± 0.002
301 ± 1	30 ± 1	1.0 : 17.0 ± 1.9 : 1.1 ± 0.1	0.78 ± 0.02
301 ± 1	66 ± 1	1.0 : 16.1 ± 0.8 : 0.97 ± 0.04	0.78 ± 0.01
301 ± 1	83 ± 1	1.0 : 12.1 ± 0.5 : 0.93 ± 0.04	0.73 ± 0.02
303 ± 1	82 ± 1	1 : 21.9 ± 1.7 : 1.5 ± 0.1	0.80 ± 0.01
303 ± 1	57 ± 2	1 : 26.3 ± 1.0 : 1.4 ± 0.1	0.83 ± 0.01
305 ± 2	69 ± 1	1.0 : 18.5 ± 0.6 : 1.1 ± 0.1	0.79 ± 0.01
309 ± 2	62 ± 5	1.0 : 36.6 ± 0.7 : 1.8 ± 0.1	0.86 ± 0.01
309 ± 2	49 ± 2	1.0 : 38.9 ± 0.7 : 1.8 ± 0.1	0.86 ± 0.01
319 ± 1	12 ± 1	1.0 : 58.3 ± 4.3 : 1.4 ± 0.05	0.92 ± 0.01

^a Percent conversions according to eq S1.

Table S8. Dependence of product distributions on temperature from irradiations of ACOB₁ in PEMA films ($T_g = 342$ K).

T [K]	percent conversion ^a	[AA]:[AB ₁]:[B ₁ B ₁] ^b	F_c
300 ± 2	53 ± 2	1.0 : 26.2 ± 1.8 : 1.6 ± 0.2	0.81 ± 0.02
300 ± 1	10 ± 1	1.0 : 35.6 ± 2.3 : 1.2 ± 0.2	0.88 ± 0.01
300 ± 1	7 ± 1	1.0 : 39.97 ± 3.2 : 1.3 ± 0.1	0.89 ± 0.01
306 ± 1	32 ± 1	1.0 : 42.3 ± 1.8 : 1.3 ± 0.1	0.90 ± 0.01
306 ± 1	12 ± 1	1.0 : 31.7 ± 2.4 : 1.3 ± 0.1	0.87 ± 0.01
310 ± 1	14 ± 1	1.0 : 37.3 ± 1.3 : 1.2 ± 0.05	0.89 ± 0.01
310 ± 1	28 ± 2	1.0 : 83.0 ± 5.1 : 1.2 ± 0.03	0.95 ± 0.003
310 ± 1	36 ± 2	1.0 : 62.6 ± 9.8 : 1.4 ± 0.1	0.92 ± 0.01
320 ± 1	18 ± 1	1.0 : 51.5. ± 1.5 : 1.4 ± 0.1	0.91 ± 0.01
320 ± 1	35 ± 1	1.0 : 89.2. ± 2.0 : 1.66 ± 0.1	0.94 ± 0.004
353 ± 1	24 ± 3	1.0 : 178.3 ± 3.4 : 1.6 ± 0.1	0.98 ± 0.001
360 ± 1	23 ± 2	[AB ₁] product	1.0
360 ± 1	54 ± 3	[AB ₁] product	1.0
365 ± 1	36 ± 9	[AB ₁] product	1.0
374 ± 1	26 ± 1	[AB ₁] product	1.0

^a Percent conversions according to eq S1. ^b [AB₁] indicates that no peaks for the AA and B₁B₁ products were detected in the GC chromatograms.

Table S9. Dependence of product distributions on temperature from irradiations of ACOB₁ in PCHMA films ($T_g = 368$ K).

T [K]	percent conversion^a	[AA]:[AB₁]:[B₁B₁]^b	F_c
307 ± 1	31 ± 1	1.0 : 389 ± 23 : 1.4 ± 0.1	0.99 ± 0.001
307 ± 1	32 ± 3	1.0 : 191 ± 30 : 1.4 ± 0.1	0.99 ± 0.01
353 ± 1	5 ± 0.3	1.0 : 315 ± 17 : 1.6 ± 0.1	0.98 ± 0.001
353 ± 1	12 ± 0.2	1.0 : 237 ± 6.2 : 1.6 ± 0.1	0.98 ± 0.001
379 ± 2	5 ± 1	[AB ₁] product	1.00
379 ± 2	72 ± 2	[AB ₁] product	1.00

^a Percent conversions according to eq S1. ^b [AB₁] indicates that no peaks for the AA and B₁B₁ products were detected in the GC chromatograms.

Table S10. Dependence of product distributions on temperature from irradiations of ACOB₁ in PIBMA films ($T_g = 322$ K)

T [K]	percent conversion^a	[AA]:[AB₁]:[B₁B₁]^b	F_c
294 ± 1	9 ± 1	1.0 : 192 ± 18 : 1.6 ± 0.1	0.97 ± 0.003
306 ± 1	11 ± 1	1.0 : 115 ± 23 : 1.7 ± 0.1	0.95 ± 0.01
306 ± 1	9 ± 1	1.0 : 72 ± 9 : 1.4 ± 0.2	0.93 ± 0.01
335 ± 1	5 ± 1	[AB ₁] product	1.0
335 ± 1	16 ± 1	[AB ₁] product	1.0
346 ± 1	13 ± 1	[AB ₁] product	1.0
355 ± 1	19 ± 1	[AB ₁] product	1.0

355 ± 1	21 ± 1	[AB ₁] product	1.0
-------------	------------	----------------------------	-----

^a Percent conversion according to eq S1. ^b [AB₁] indicates that no peaks for the AA and B₁B₁ products were detected in the chromatograms.

2. References

- (1) C. A. Chesta, J. Mohanty, W. M. Nau, U. Bhattacharjee, R. G. Weiss, *J. Am. Chem. Soc.* 2007, **129**, 5012.
- (2) J. R. Taylor, *An Introduction to Error Analysis: The Study of Uncertainties in Physical Measurements*; University Science Books: Sausalito, California, 1982.
- (3) H. Langhals, H. Fischer, *Chem. Ber.* 1978, **111**, 543.