Aggregation and Reactivity of the Lithium Enolate of 2-Biphenylylcyclohexanone in Tetrahydrofuran

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Supporting Information

Table S1. Computed structures of the lithium enolates of phenylcyclohexanone (xyz coordinates at HF 6-31+G*.

Conjugated enolate:

C	1.597165	0.095286	1.203919
C	0.873713	-0.294068	0.068615
C	1.611308	-0.635794	-1.071410
C	3.001552	-0.586406	-1.081558
C	3.696754	-0.185800	0.051976
C	2.987921	0.152502	1.197812
C	-0.622144	-0.249987	0.048130
C	-1.381496	-1.542676	0.270111
C	-2.850912	-1.418746	-0.136654
C	-3.448369	-0.117099	0.392283
C	-2.712604	1.090244	-0.188903
C	-1.206262	0.948802	-0.175556
O	-0.541291	2.044336	-0.407716
Li	1.175316	2.012001	-0.433396
H	-2.960461	1.996868	0.355127
H	-3.019235	1.264325	-1.219422
H	-3.369143	-0.104160	1.478252
H	-4.508294	-0.057403	0.156303
H	-2.926833	-1.430645	-1.222793
H	-3.412298	-2.275435	0.229272
H	-1.321972	-1.851543	1.316607
H	-0.918310	-2.349534	-0.297419
H	1.082072	-0.933583	-1.959399
H	3.538656	-0.855804	-1.974132
H	4.771345	-0.144840	0.045144
H	3.514013	0.453493	2.086990

H	1.055096	0.360021	2.094802

Unconjugated enolate:

C	-0.641138	-0.321872	-0.574738
C	-1.414407	-1.501981	0.030094
C	-2.914193	-1.319331	-0.186037
C	-3.406147	-0.051835	0.513732
C	-2.493584	1.126970	0.268149
C	-1.250743	1.045433	-0.221191
C	0.836499	-0.337507	-0.208055
C	1.255435	-0.149591	1.114800
C	2.602019	-0.078365	1.439261
C	3.573112	-0.191947	0.447651
C	3.177116	-0.382603	-0.865982
C	1.821633	-0.451618	-1.186976
H	-0.691876	-0.408531	-1.659156
O	-0.461851	2.060303	-0.461556
Li	1.227684	2.061767	-0.372881
H	-2.876379	2.110444	0.488725
H	-4.411460	0.181640	0.167763
H	-3.503642	-0.248518	1.583499
H	-3.453886	-2.190080	0.179346
H	-3.115678	-1.247619	-1.253363
H	-1.067876	-2.433182	-0.412850
H	-1.214574	-1.569822	1.097237
H	0.517145	-0.035396	1.888438
H	1.529912	-0.593201	-2.213020
H	3.914044	-0.478746	-1.643788
H	4.616817	-0.137386	0.700250
H	2.895608	0.068161	2.463765

Table S2. Formal concentrations, {LiBPCH}, maximum absorption wavelengths, the maximum absorptions, and the absorptions at the isosbestic point (371.5 nm)

Wavelength λ_{max} (nm)[a]	{LiBPCH} (M)[b]	Abs.[c] λ_{max}	Abs.[d] $\lambda_{isosbestic}$	[Monomer][e] M	[Dimer][e] M
Expt 1	(1 mm cell)				
361.5	1.00E-03	2.1089	1.9974	2.82E-04	3.71E-04
362.0	8.70E-04	1.8077	1.7263	2.62E-04	3.14E-04
362.5	7.85E-04	1.6099	1.5424	2.45E-04	2.74E-04
363.0	6.99E-04	1.4266	1.3724	2.30E-04	2.39E-04
363.5	6.42E-04	1.3049	1.2608	2.19E-04	2.16E-04
363.5	5.82E-04	1.1767	1.1423	2.07E-04	1.91E-04
364.0	5.24E-04	1.0573	1.0310	1.96E-04	1.68E-04
364.0	4.84E-04	0.9712	0.9476	1.87E-04	1.51E-04
365.5	4.38E-04	0.8778	0.8624	1.76E-04	1.34E-04
364.5	3.93E-04	0.7851	0.7733	1.65E-04	1.17E-04
367.0	3.47E-04	0.6901	0.6833	1.53E-04	1.00E-04
368.0	3.00E-04	0.5952	0.5913	1.39E-04	8.35E-05
369.0	2.60E-04	0.5168	0.5141	1.27E-04	6.93E-05
370.0	2.15E-04	0.4265	0.4257	1.12E-04	5.40E-05
Expt 2	(1 mm cell)				
363	7.43E-04	1.496	1.4419	2.34E-04	2.53E-04
363.5	6.26E-04	1.2476	1.2056	2.10E-04	2.05E-04
364	5.45E-04	1.0875	1.0561	1.95E-04	1.74E-04
364	4.63E-04	0.9127	0.8942	1.76E-04	1.42E-04
365	4.17E-04	0.8216	0.8076	1.65E-04	1.25E-04
365	3.73E-04	0.7312	0.721	1.53E-04	1.08E-04
367.5	3.22E-04	0.6295	0.6244	1.40E-04	9.06E-05
369	2.86E-04	0.5558	0.5524	1.29E-04	7.72E-05
369.5	2.48E-04	0.4839	0.4816	1.18E-04	6.47E-05
370	2.30E-04	0.4485	0.4477	1.13E-04	5.85E-05
370	2.00E-04	0.3901	0.3891	1.02E-04	4.87E-05
370.5	1.81E-04	0.35	0.3498	9.55E-05	4.21E-05
371	1.61E-04	0.3117	0.3117	8.86E-05	3.57E-05
371	1.36E-04	0.2631	0.2631	7.86E-05	2.80E-05
373	1.12E-04	0.2189	0.2188	6.92E-05	2.14E-05

Expt 3	(1 cm cell)				
374	1.04E-04	2.3273	2.3194	7.53E-05	2.28E-05
375	9.87E-05	2.201	2.1886	7.24E-05	2.11E-05
375	9.12E-05	2.0302	2.0164	6.81E-05	1.89E-05
375.5	8.43E-05	1.8843	1.8658	6.43E-05	1.69E-05
376	8.04E-05	1.7945	1.7782	6.21E-05	1.57E-05
376	7.60E-05	1.6981	1.6792	5.94E-05	1.45E-05
377	7.10E-05	1.5895	1.5681	5.65E-05	1.31E-05
377	6.55E-05	1.471	1.4496	5.32E-05	1.17E-05
377.5	6.14E-05	1.3855	1.3611	5.07E-05	1.07E-05
378	5.74E-05	1.2982	1.2701	4.81E-05	9.62E-06
378.5	5.39E-05	1.2247	1.1955	4.60E-05	8.73E-06
379	5.02E-05	1.1451	1.1141	4.34E-05	7.87E-06
379	4.61E-05	1.0583	1.0249	4.08E-05	6.89E-06
379.5	4.32E-05	0.9948	0.9622	3.88E-05	6.25E-06
380.5	3.99E-05	0.9241	0.8889	3.64E-05	5.50E-06
381	3.72E-05	0.8664	0.8299	3.46E-05	4.90E-06
381	3.37E-05	0.7921	0.7558	3.20E-05	4.22E-06
382	2.99E-05	0.7082	0.6725	2.90E-05	3.49E-06
382	2.63E-05	0.6284	0.5925	2.61E-05	2.84E-06
382.5	2.36E-05	0.57	0.5356	2.39E-05	2.39E-06

a. maximum absorption wavelength of LiBPCH.

b. formal concentration of LiBPCH calculated on the basis of the weight of BPCH and THF.

c. absorbance at λ_{max}.

d. absorbance at the isosbestic point 371.5 nm.

e. [Monomer] and [Dimer] calculated from the spectra in Figure 2. Note that [M] +2[D] does not necessarily add up to exactly {LiBPCH}.

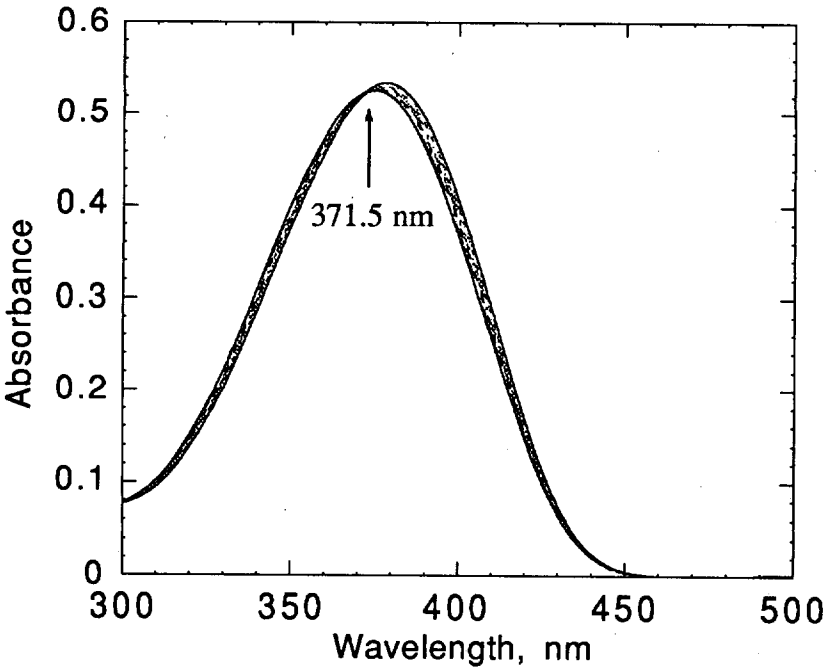

Figure S1. Superposition of 9 normalized spectra of LiBPCH showing isosbestic point at 371.5 nm.

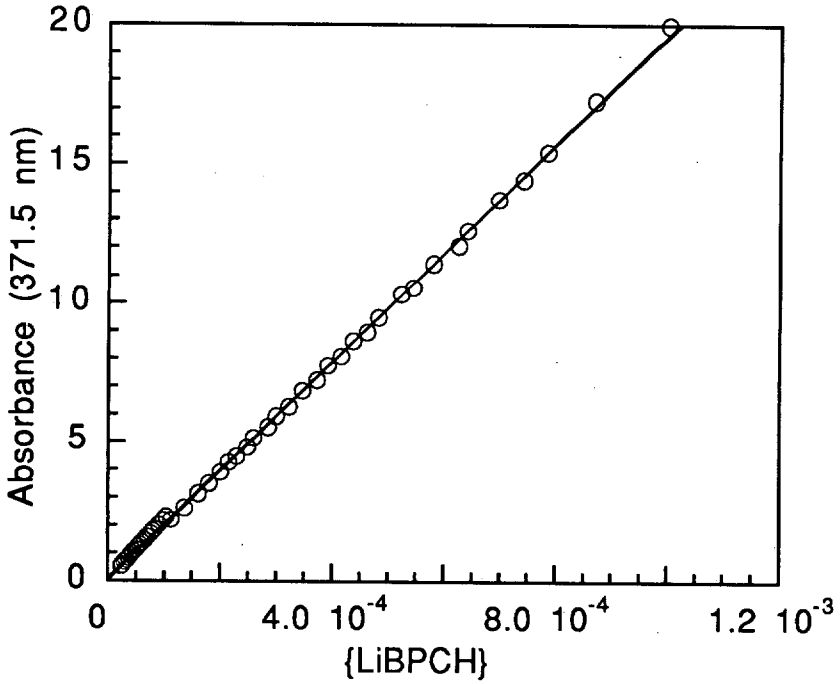

Figure S2. Absorbance for 1 cm pathlength at isosbestic point, 371.5 nm. The line shown is (0.094 ± 0.025) + (19471 ± 65)x. The extinction coefficient is 19471. A similar plot for the absorbance at λ_{max} gives ε = 20308.

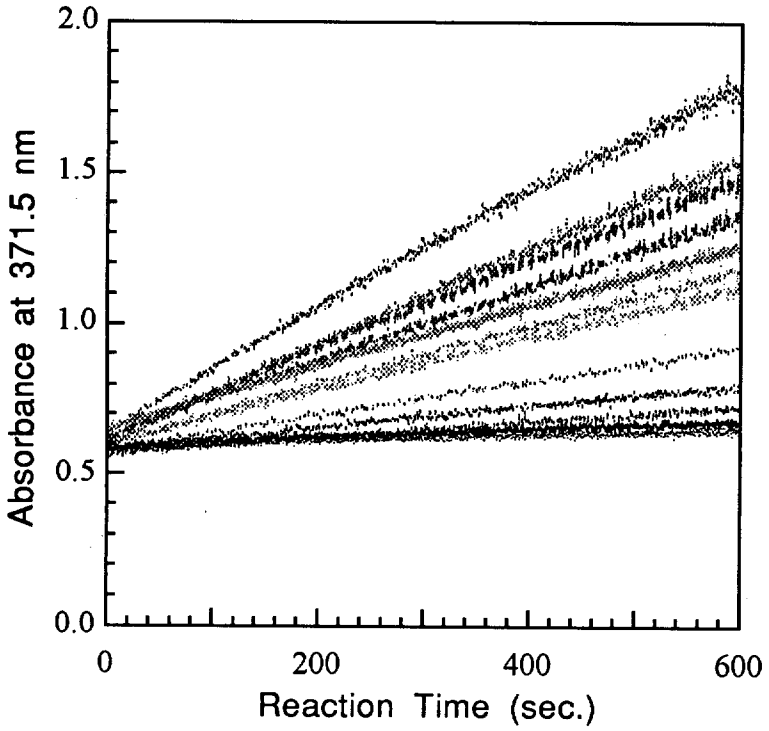

Figure S3. Spectrometer scans at the isosbestic point for several runs showing the growth of LiBPCH with time. Initial slopes were used for the kinetics analyses.

Table S3. Rates of conversion of unconjugated to conjugated enolate at 25 °C in THF.

[Unconj enolate, **1**], M	[BPCH], M	reaction rate $M^{-1}\ s^{-1}$
1.306E-03	4.447E-05	8.501E-08
1.306E-03	5.873E-05	1.020E-07
1.306E-03	9.396E-05	1.532E-07
1.306E-03	1.263E-04	2.095E-07
1.306E-03	1.938E-04	3.168E-07
1.306E-03	2.686E-04	4.853E-07
1.306E-03	3.086E-04	5.331E-07
1.306E-03	3.344E-04	6.733E-07
1.306E-03	4.415E-04	8.903E-07
1.306E-03	4.934E-04	1.098E-06
1.306E-03	2.540E-04	5.549E-07
1.951E-03	2.860E-04	3.833E-07
2.140E-03	2.860E-04	3.966E-07
6.500E-04	2.860E-04	3.222E-07
7.834E-04	2.860E-04	3.472E-07
4.339E-03	2.860E-04	4.767E-07
2.991E-03	2.860E-04	4.732E-07

1.324E-03	2.860E-04	3.934E-07
2.513E-03	2.860E-04	4.400E-07
2.564E-03	2.860E-04	4.562E-07
2.433E-03	2.860E-04	4.385E-07
4.176E-04	2.860E-04	2.646E-07
4.787E-04	2.860E-04	2.841E-07
1.044E-03	2.860E-04	3.407E-07

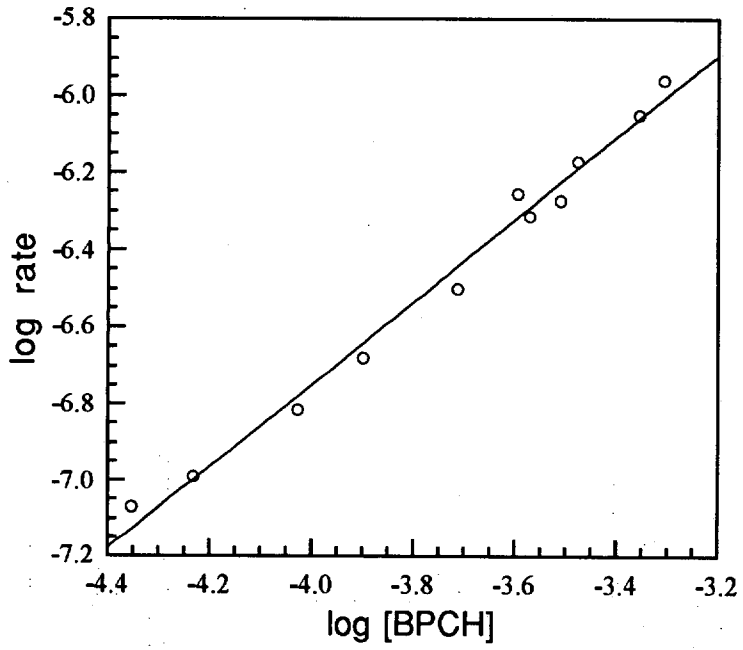

Figure S4. Log-log plot of the initial rate of conversion of **1** to LiBPCH with varying ketone concentration and constant [**1**]. The slope of the regression line shown is 1.07 ± 0.04.

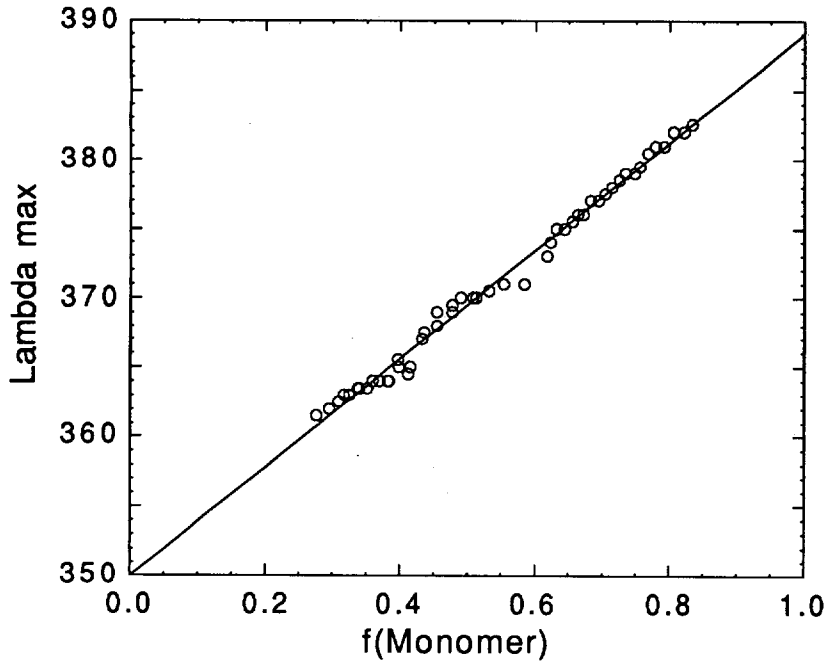

Figure S5. Plot of the λ_{max} of each spectrum in Table S2 vs the fraction monomer using the values recorded in Table S2. The regression line shown is 350.1 + 39.1x, R^2 = 0.992.

Table S4. $K_{1,2}$ as a function of temperature.

Temperature, °C	$K_{1,2}$ M^{-1}
25	3935
20	4038
15	4178
10	4368
5	4576
0	4831

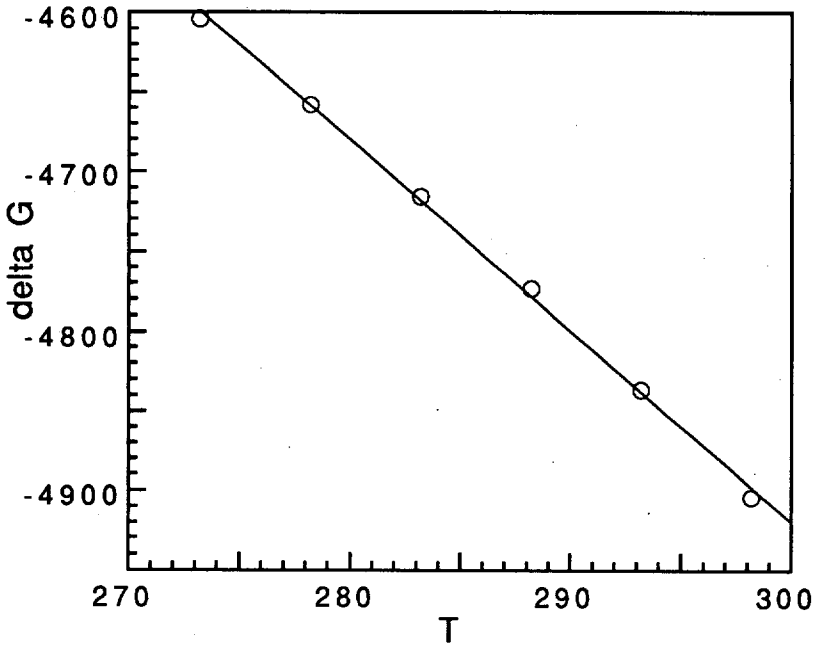

Figure S6. Plot of $\Delta G°$ (kcal mol^{-1}) vs absolute temperature of the monomer-dimer equilibrium of LiBPCH. The line shown corresponds to $\Delta H° = -1.33 \pm 0.65$ kcal mol^{-1}.

Table S5. Ion Pair acidity

{LiBPCH} M	{LiDPI} M	[BPCH] M	[DPI] M	K_{ob}	K_{corr}	pKa
2.962E-5	3.571E-5	1.878E-3	1.638E-3	0.7234	1.221	12.23
4.497E-5	4.638E-5	1.863E-3	1.628E-3	0.8470	1.342	12.19
6.566E-5	5.954E-5	1.842E-3	1.614E-3	0.9663	1.452	12.16
9.954E-5	7.763E-5	1.808E-3	1.596E-3	1.132	1.617	12.11
1.260E-4	9.046E-5	1.782E-3	1.584E-3	1.238	1.724	12.08
1.504E-4	1.007E-4	1.758E-3	1.573E-3	1.337	1.831	12.06
1.805E-4	1.133E-4	1.728E-3	1.561E-3	1.440	1.936	12.03
2.115E-4	1.286E-4	1.697E-3	1.545E-3	1.499	1.979	12.02
2.517E-4	1.442E-4	1.656E-3	1.530E-3	1.612	2.096	12.00
2.835E-4	1.570E-4	1.624E-3	1.517E-3	1.686	2.169	11.98
3.392E-4	1.750E-4	1.569E-3	1.499E-3	1.852	2.350	11.95

3.875E-4	1.929E-4	1.520E-3	1.481E-3	1.957	2.457	11.93
4.602E-4	2.189E-4	1.448E-3	1.455E-3	2.113	2.615	11.90
5.436E-4	2.452E-4	1.364E-3	1.429E-3	2.321	2.840	11.87
6.377E-4	2.806E-4	1.270E-3	1.393E-3	2.493	3.010	11.84

Table S6. Reaction kinetics of LiBPCH with methyl brosylate in THF at 25 °C.

Run	[MeOBs], M	{LiBPCH}, M	init rate, M s^{-1}	[Monomer], M	[Dimer], M
1	0.0212	9.60E-04	1.56E-07	2.81E-04	3.39E-04
2	0.0192	9.16E-04	1.41E-07	2.73E-04	3.21E-04
3	0.0160	9.28E-04	1.18E-07	2.75E-04	3.26E-04
4	0.0151	9.17E-04	1.17E-07	2.74E-04	3.22E-04
5	0.0124	9.15E-04	9.35E-08	2.73E-04	3.21E-04
6	0.0111	9.75E-04	8.49E-08	2.84E-04	3.46E-04
7	0.0144	9.71E-04	1.07E-07	2.83E-04	3.44E-04
8	0.0196	9.27E-04	1.38E-07	2.75E-04	3.26E-04
9	0.0243	9.66E-04	1.72E-07	2.82E-04	3.42E-04
10	0.0282	9.26E-04	1.88E-07	2.75E-04	3.26E-04
11	0.0318	9.47E-04	2.14E-07	2.79E-04	3.34E-04
12	0.0357	9.35E-04	2.36E-07	2.77E-04	3.29E-04
13	0.0151	6.71E-04	9.34E-08	2.27E-04	2.22E-04
14	0.0249	6.85E-04	1.50E-07	2.30E-04	2.27E-04
15	0.0320	6.71E-04	1.94E-07	2.27E-04	2.22E-04
16	0.0505	6.74E-04	2.94E-07	2.28E-04	2.23E-04
17	0.0379	6.15E-04	2.14E-07	2.16E-04	2.00E-04
18	0.0583	6.41E-04	3.25E-07	2.21E-04	2.10E-04
19	0.0429	6.59E-04	2.39E-07	2.25E-04	2.17E-04
20	0.0296	6.57E-04	1.70E-07	2.24E-04	2.17E-04
21	0.0203	6.61E-04	1.21E-07	2.25E-04	2.18E-04
22	0.0069	6.54E-04	3.84E-08	2.24E-04	2.15E-04
23	0.0108	6.30E-04	6.57E-08	2.19E-04	2.05E-04
24	0.0147	2.79E-04	8.78E-08	1.31E-04	7.39E-05
25	0.0147	5.79E-04	1.37E-07	2.08E-04	1.85E-04
26	0.0238	7.36E-04	1.54E-07	2.40E-04	2.48E-04
27	0.0238	4.24E-04	1.11E-07	1.71E-04	1.26E-04
28	0.0238	1.94E-04	7.00E-08	1.03E-04	4.57E-05

29	0.0238	1.15E-04	4.98E-08	7.13E-05	2.19E-05
30	0.0238	3.39E-04	9.55E-08	1.49E-04	9.50E-05
31	0.0238	5.13E-04	1.25E-07	1.93E-04	1.60E-04
32	0.0238	6.21E-04	1.39E-07	2.17E-04	2.02E-04
33	0.0238	6.65E-04	1.43E-07	2.26E-04	2.19E-04
34	0.0238	7.95E-04	1.59E-07	2.51E-04	2.72E-04
35	0.0238	5.07E-04	1.24E-07	1.91E-04	1.58E-04
36	0.0238	2.69E-04	8.26E-08	1.28E-04	7.05E-05

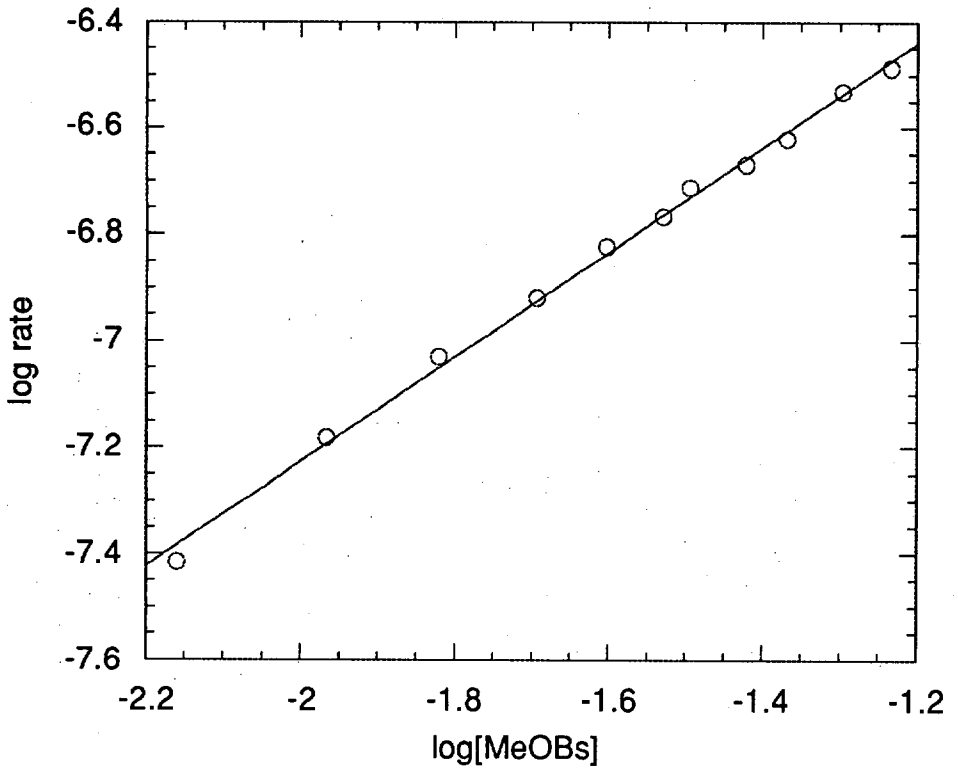

Figure S7. Log-log plot of rate vs [MeOBs] at constant {LiBPCH} = 6.6 x 10^{-4} M; slope = 0.98 ± 0.02.

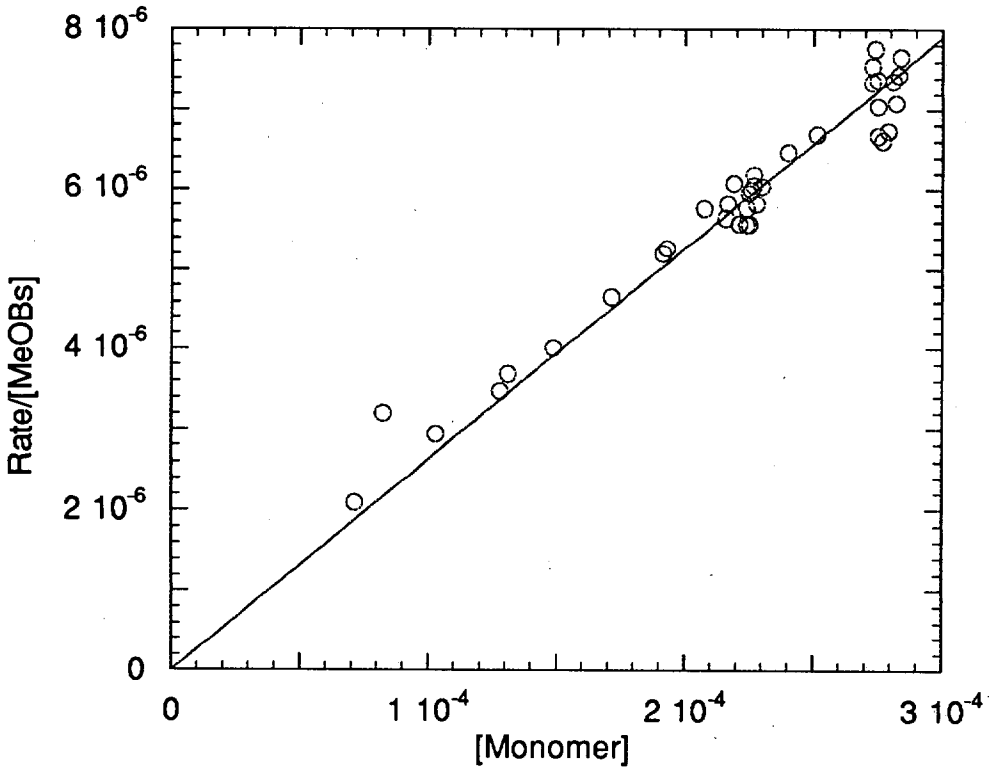

Fig S8. Rate/[MeOBs] compared to [Monomer]; Line shown through the origin has slope = 0.0263 ± 0.0002; R^2 = 0.947. This slope is k_2, M^{-1} s^{-1}.

Table S7. Kinetics of Reaction of LiBPCH with benzyl bromides in THF at 25 °C.

[BnBr], M	{LiBPCH}, M	init rate, M s^{-1}	[Monomer], M	Dimer, M
Benzyl Bromide				
0.00940	7.92E-04	1.95E-06	2.51E-04	2.70E-04
0.00940	8.87E-04	1.87E-06	2.68E-04	3.09E-04
0.00940	2.68E-04	9.24E-07	1.28E-04	7.02E-05
0.00940	1.65E-04	6.42E-07	9.20E-05	3.64E-05
0.00940	5.92E-04	1.55E-06	2.11E-04	1.91E-04
0.00940	4.24E-04	1.36E-06	1.71E-04	1.26E-04
0.00940	6.30E-04	1.63E-06	2.19E-04	2.06E-04
0.00940	7.32E-04	1.82E-06	2.39E-04	2.46E-04
0.00940	7.06E-04	1.62E-06	2.34E-04	2.36E-04
0.00940	5.41E-04	1.48E-06	1.99E-04	1.71E-04
0.00940	3.86E-04	1.16E-06	1.62E-04	1.12E-04
0.00940	3.06E-04	9.70E-07	1.39E-04	8.34E-05
0.00940	2.39E-04	8.26E-07	1.18E-04	6.02E-05

0.00940	8.39E-05	4.57E-07	5.65E-05	1.37E-05
0.00940	4.32E-04	1.20E-06	1.73E-04	1.29E-04
o-Chlorobenzyl Bromide				
0.0140	3.24E-04	1.05E-06	1.45E-04	8.99E-05
0.0583	4.48E-04	1.24E-06	1.77E-04	1.35E-04
0.0429	6.07E-04	1.63E-06	2.14E-04	1.97E-04
0.0296	7.55E-04	1.94E-06	2.44E-04	2.56E-04
0.0203	8.96E-04	2.05E-06	2.70E-04	3.13E-04
0.0069	2.37E-04	9.03E-07	1.18E-04	5.95E-05
0.0108	4.00E-04	1.12E-06	1.65E-04	1.17E-04
0.0147	1.20E-04	5.70E-07	7.33E-05	2.31E-05
0.0147	1.58E-04	6.42E-07	8.92E-05	3.42E-05
0.0238	2.94E-04	9.34E-07	1.36E-04	7.91E-05
0.0238	6.06E-04	1.20E-06	2.14E-04	1.96E-04
0.0238	6.20E-04	1.67E-06	2.17E-04	2.02E-04
0.0238	7.67E-04	1.27E-06	2.46E-04	2.60E-04
0.0238	5.19E-04	1.21E-06	1.94E-04	1.62E-04
0.0238	9.26E-04	1.89E-06	2.75E-04	3.25E-04
m-Chlorobenzyl Bromide				
0.00858	2.78E-04	1.66E-06	1.31E-04	7.37E-05
0.00858	3.40E-04	1.83E-06	1.49E-04	9.54E-05
0.00858	4.26E-04	2.13E-06	1.72E-04	1.27E-04
0.00858	2.81E-04	1.64E-06	1.32E-04	7.45E-05
0.00858	2.05E-04	1.32E-06	1.07E-04	4.90E-05
0.00858	1.50E-04	1.07E-06	8.60E-05	3.18E-05
0.00858	8.02E-04	3.22E-06	2.53E-04	2.75E-04
0.00858	7.09E-04	2.95E-06	2.35E-04	2.37E-04
0.00858	5.71E-04	2.51E-06	2.06E-04	1.83E-04
0.00858	4.43E-04	2.25E-06	1.76E-04	1.33E-04
0.00858	3.11E-04	1.62E-06	1.41E-04	8.52E-05
0.00858	6.79E-04	2.84E-06	2.29E-04	2.25E-04
0.00858	5.54E-04	2.57E-06	2.02E-04	1.76E-04
0.00858	8.97E-04	3.59E-06	2.70E-04	3.13E-04
0.00858	1.01E-04	8.62E-07	6.50E-05	1.81E-05
o-Methylbenzyl bromide				
0.0205	2.83E-04	1.82E-06	1.32E-04	7.54E-05

0.0205	4.48E-04	2.55E-06	1.78E-04	1.35E-04
0.0205	5.60E-04	3.43E-06	2.04E-04	1.78E-04
0.0205	6.65E-04	3.63E-06	2.26E-04	2.19E-04
0.0205	2.39E-04	1.71E-06	1.18E-04	6.02E-05
0.0205	7.73E-04	3.81E-06	2.47E-04	2.63E-04
0.0205	1.43E-04	1.10E-06	8.34E-05	2.99E-05
0.0205	9.33E-04	3.74E-06	2.76E-04	3.28E-04
0.0205	8.44E-04	3.46E-06	2.61E-04	2.92E-04
0.0205	6.20E-04	2.81E-06	2.17E-04	2.02E-04
0.0205	6.08E-04	2.75E-06	2.14E-04	1.97E-04
0.0205	4.40E-04	2.25E-06	1.75E-04	1.32E-04
0.0205	2.54E-04	1.90E-06	1.23E-04	6.53E-05
0.0205	2.23E-04	1.45E-06	1.13E-04	5.50E-05
0.0205	5.30E-05	6.11E-07	3.96E-05	6.73E-06
0.0205	1.63E-04	1.26E-06	9.12E-05	3.58E-05
0.0205	4.91E-04	2.64E-06	1.88E-04	1.52E-04

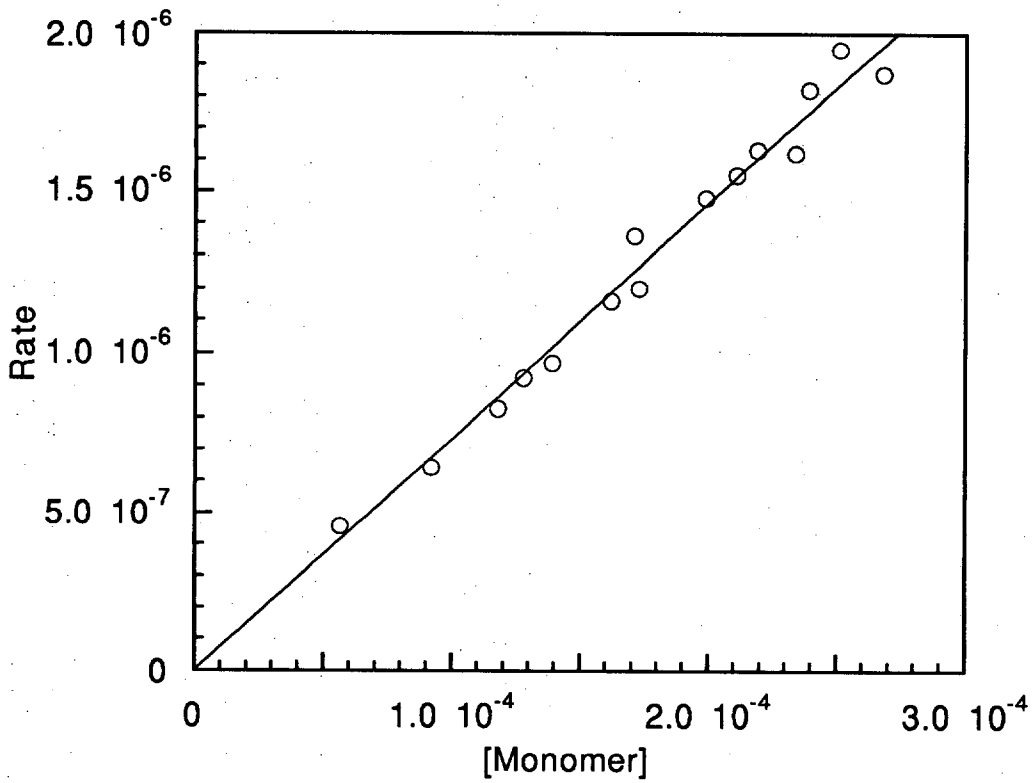

Figure S9. Rate of benzyl bromide (0.00940M) vs concentration of monomer Slope of line through the origin is (0.732 ± 0.09) x 10^{-3}; k_2 = 0.779 M^{-1} s^{-1}.

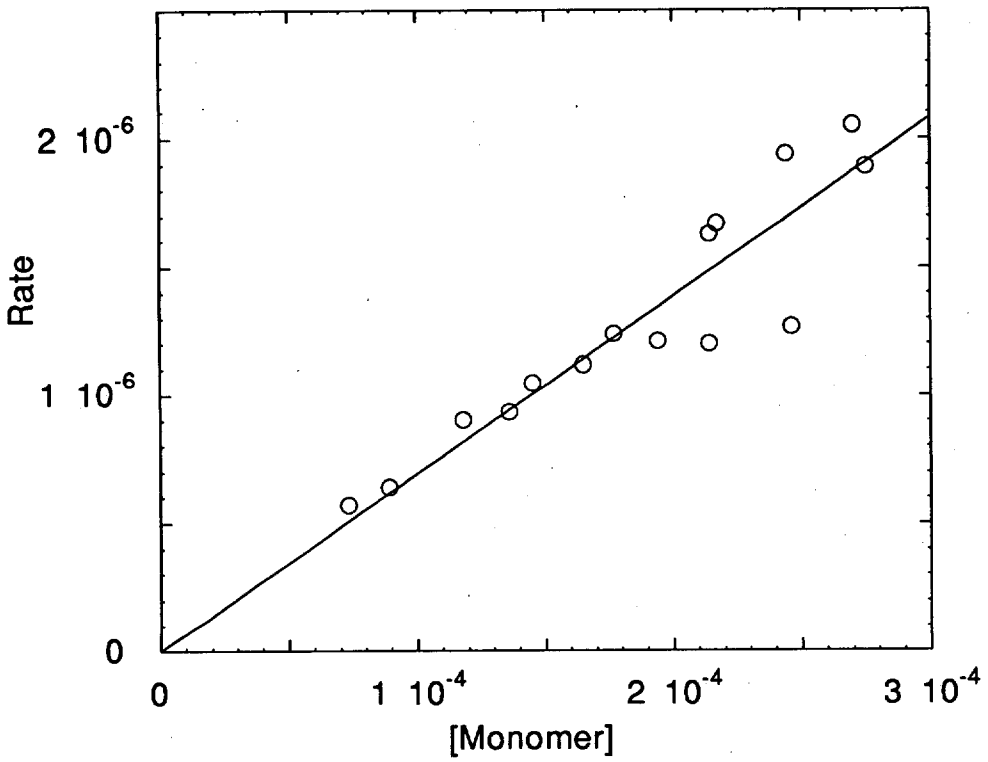

Figure S10. Rate of o-chlorobenzyl bromide (0.0140M) vs concentration of monomer Slope of line through the origin is (6.93 ± 0.24) x 10^{-3}; k_2 = 0.50 M^{-1} s^{-1}.

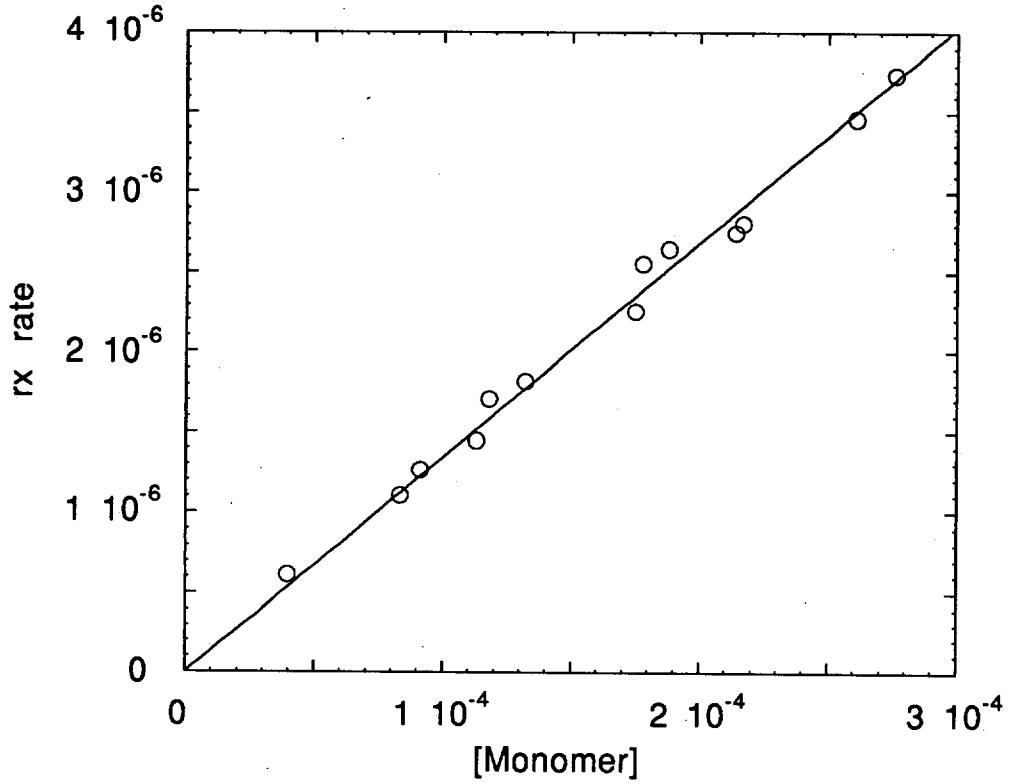

Figure S11. Rate of o-methylbenzyl bromide (0.0205M) vs concentration of monomer. Slope of line through the origin is (13.4 ± 0.2) x 10^{-3}; k_2 = 0.655 M^{-1} s^{-1}.

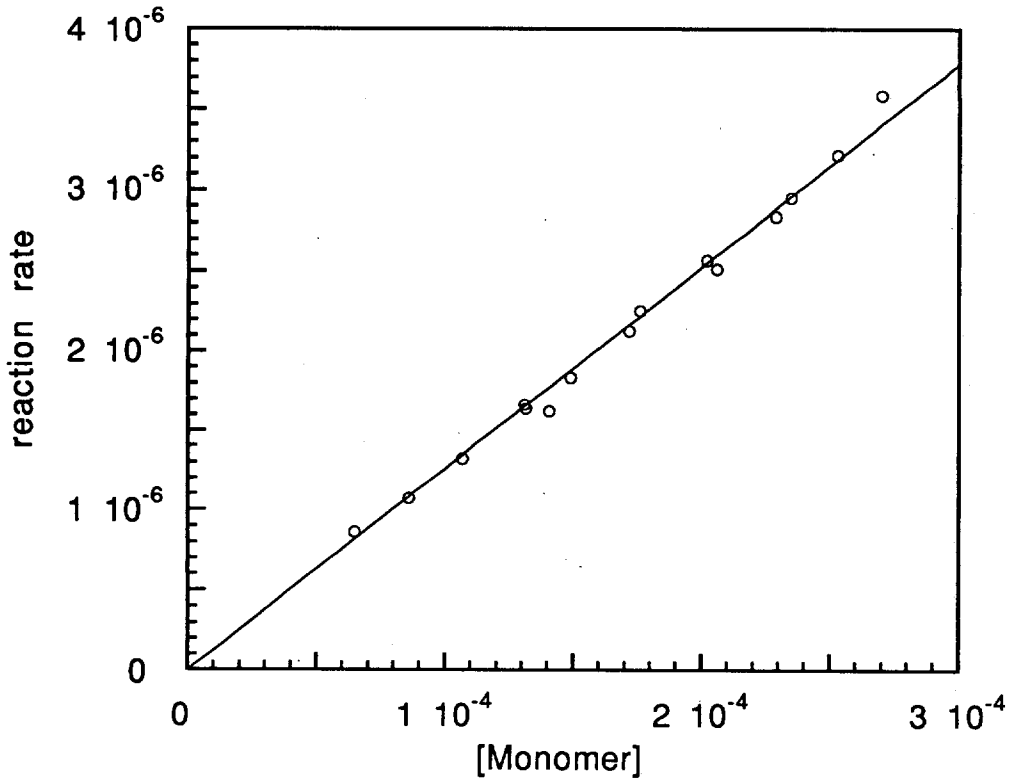

Figure S12. Rate of m-chlorobenzyl bromide (0.00858M) vs concentration of monomer. Slope of line through the origin is (12.6 ± 0.1) x 10^{-3}; k_2 = 1.47 M^{-1} s^{-1}.

Table S8. Reaction of m-chlorobenzyl bromide in the presence of $LiBPh_4$.

[$LiBPh_4$], M	[mClBnBr], M	{LiBPCH}, M	rate	[Monomer], M	[Dimer], M
4.887E-5	8.596E-3	6.49E-04	3.10E-06	2.23E-04	2.13E-04
4.887E-5	8.596E-3	4.42E-04	2.54E-06	1.76E-04	1.33E-04
4.887E-5	8.596E-3	4.28E-04	2.49E-06	1.72E-04	1.28E-04
4.887E-5	8.596E-3	8.15E-04	4.09E-06	2.55E-04	2.80E-04
4.887E-5	8.596E-3	9.16E-04	4.21E-06	2.73E-04	3.21E-04
4.887E-5	8.596E-3	5.43E-04	3.01E-06	2.00E-04	1.71E-04
4.887E-5	8.596E-3	3.38E-04	2.10E-06	1.48E-04	9.48E-05
4.887E-5	8.596E-3	2.57E-04	1.74E-06	1.24E-04	6.65E-05
9.66E-5	8.60E-3	6.70E-04	3.35E-06	2.27E-04	1.09E-02
9.66E-5	8.60E-3	1.10E-03	4.76E-06	3.04E-04	9.38E-03
9.66E-5	8.60E-3	1.00E-03	4.31E-06	2.88E-04	9.63E-03
9.66E-5	8.60E-3	8.80E-04	3.53E-06	2.67E-04	1.00E-02
9.66E-5	8.60E-3	5.77E-04	2.81E-06	2.07E-04	1.14E-02
9.66E-5	8.60E-3	4.70E-04	2.45E-06	1.83E-04	1.21E-02

9.66E-5	8.60E-3	3.75E-04	2.20E-06	1.59E-04	1.30E-02
9.66E-5	8.60E-3	2.98E-04	1.88E-06	1.37E-04	1.40E-02
9.66E-5	8.60E-3	1.67E-04	1.28E-06	9.28E-05	1.70E-02
9.66E-5	8.60E-3	3.91E-04	2.04E-06	1.63E-04	1.28E-02
9.66E-5	8.60E-3	8.85E-04	3.63E-06	2.68E-04	9.99E-03
5.19E-4	8.59E-3	6.42E-04	3.25E-06	2.21E-04	2.10E-04
5.19E-4	8.59E-3	9.34E-04	4.17E-06	2.76E-04	3.29E-04
5.19E-4	8.59E-3	7.74E-04	3.63E-06	2.47E-04	2.63E-04
5.19E-4	8.59E-3	4.95E-04	2.55E-06	1.89E-04	1.53E-04
5.19E-4	8.59E-3	3.70E-04	2.04E-06	1.57E-04	1.06E-04
5.19E-4	8.59E-3	2.31E-04	1.52E-06	1.16E-04	5.78E-05
5.19E-4	8.59E-3	1.55E-04	1.15E-06	8.83E-05	3.35E-05
5.19E-4	8.59E-3	5.41E-04	2.51E-06	1.99E-04	1.71E-04
9.07E-3	8.59E-3	6.14E-04	3.63E-06	2.15E-04	1.99E-04
9.07E-3	8.59E-3	4.97E-04	3.23E-06	1.89E-04	1.54E-04
9.07E-3	8.59E-3	4.06E-04	2.86E-06	1.67E-04	1.20E-04
9.07E-3	8.59E-3	2.90E-04	2.28E-06	1.34E-04	7.77E-05
9.07E-3	8.59E-3	1.84E-04	1.59E-06	9.94E-05	4.25E-05
9.07E-3	8.59E-3	1.48E-03	7.32E-06	3.61E-04	5.59E-04

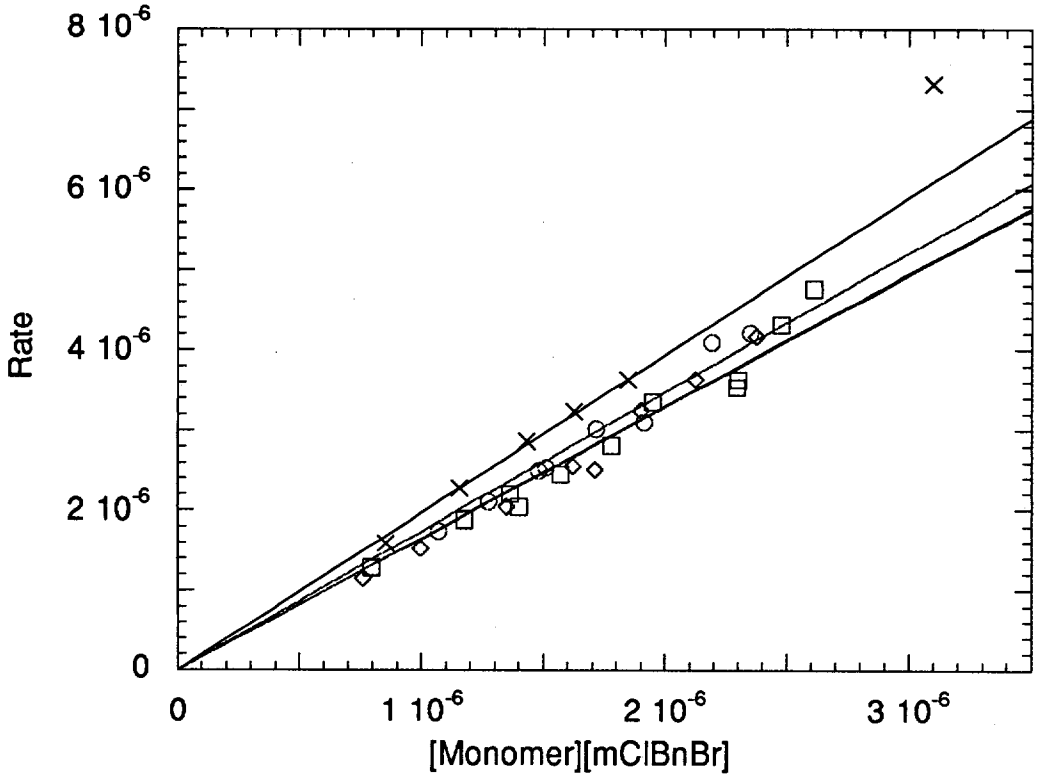

Figure S13. Rates of reaction of LiBPCH with m-chlorobenzyl bromide at 25 °C with added $LiBPh_4$. Equations for lines shown are the second order rate constants for the monomer, $M^{-1}\ s^{-1}$: circles, $[LiBPh_4] = 4.89 \times 10^{-5}M$, rate = 1.74 ± 0.03; squares, $[LiBPh_4] = 9.66 \times 10^{-5}M$, rate = 1.65 ± 0.04; diamonds, $[LiBPh_4] = 5.19 \times 10^{-4}M$, rate = 1.64 ± 0.04; crosses, $[LiBPh_4] = 9.07 \times 10^{-3}M$, rate = 1.97 ± 0.02.

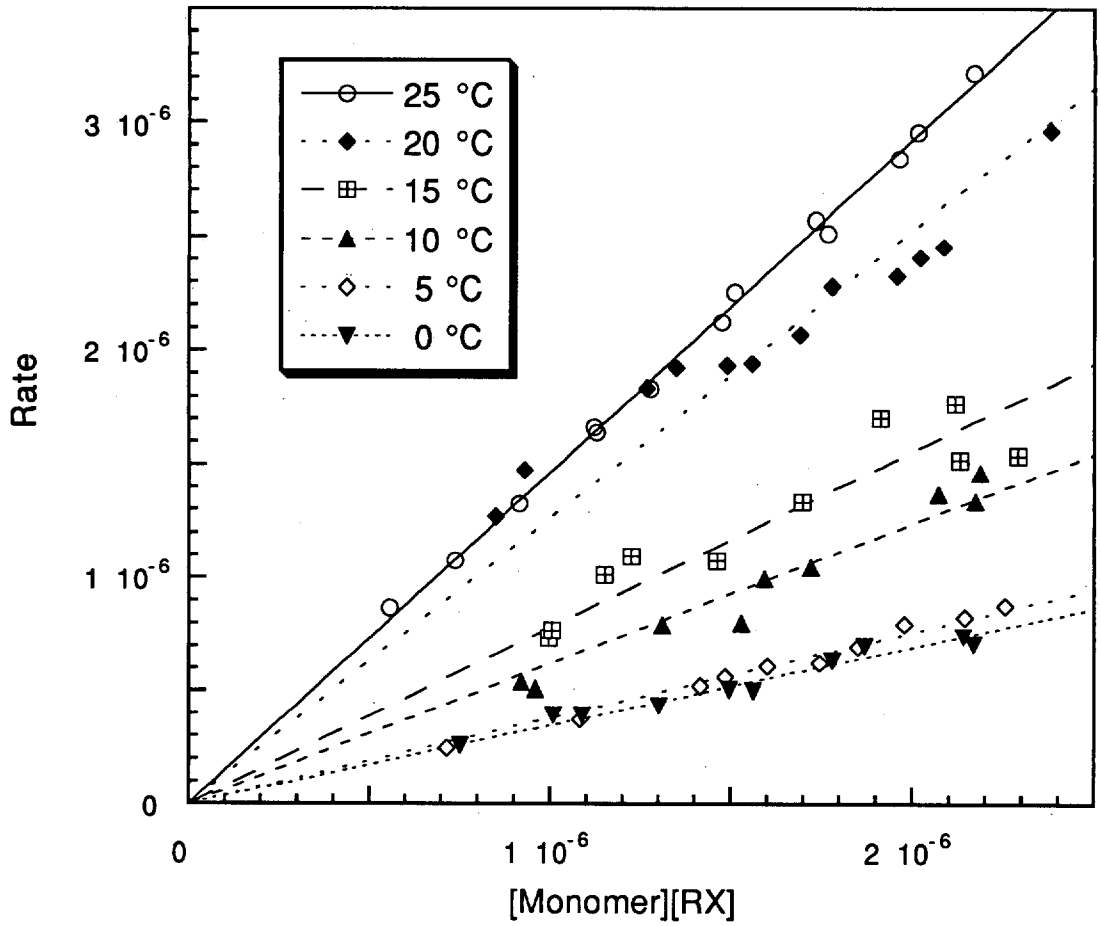

Figure S14. Initial rates of reaction (M^{-1} s^{-1}) of m-chlorobenzyl bromide with monomeric LiBPCH at various temperatures compared to initial monomer LiBPCH and alkyl bromide concentrations: circles, 25 °C; ; filled diamonds, 20 °C; squares, 15 °C; upright triangles, 10 °C; open diamonds, 5 °C; inverted triangles, 0 °C.

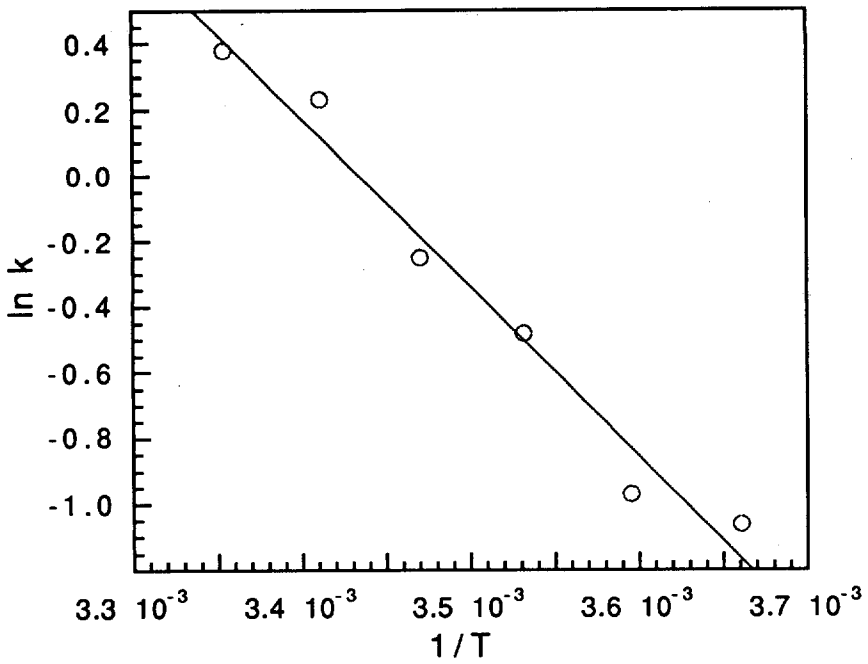

Figure S15. Plot of ln(k_2) for reaction of LiBPCH monomer with m-chlorobenzyl bromide vs 1/T. The line shown is (17.62 ± 1.52) - (5131 ± 435)/T.