

Supplementary Information

Radical Ring-Opening Polymerization of Five-Membered Cyclic Ketene Acetals with Tetraleucine Macromonomer Toward Preparation of Self-Assembling Peptide-Grafted Polyester

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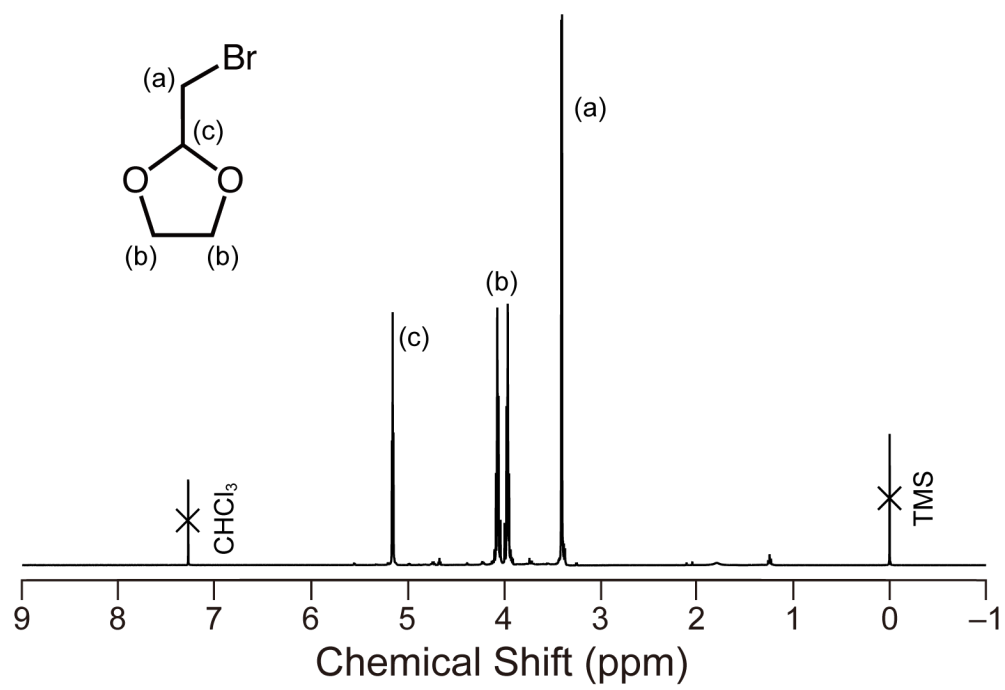


Figure S1. ^1H NMR spectrum of 2-bromomethyl-1,3-dioxolane in CDCl_3 at 25 °C.

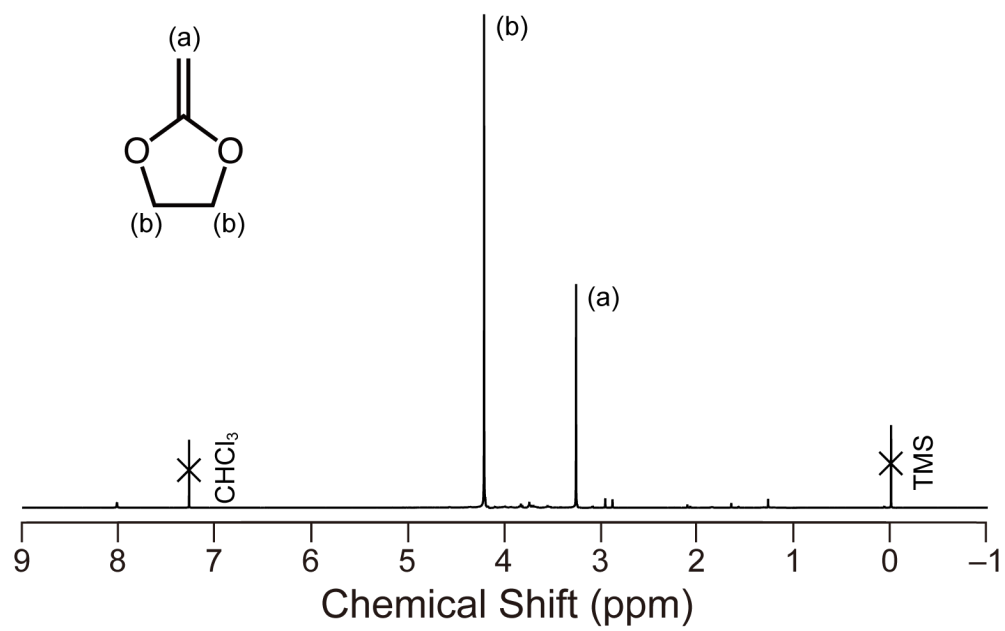


Figure S2. ¹H NMR spectrum of 2-methylene-1,3-dioxolane (C5) in CDCl₃ at 25 °C.

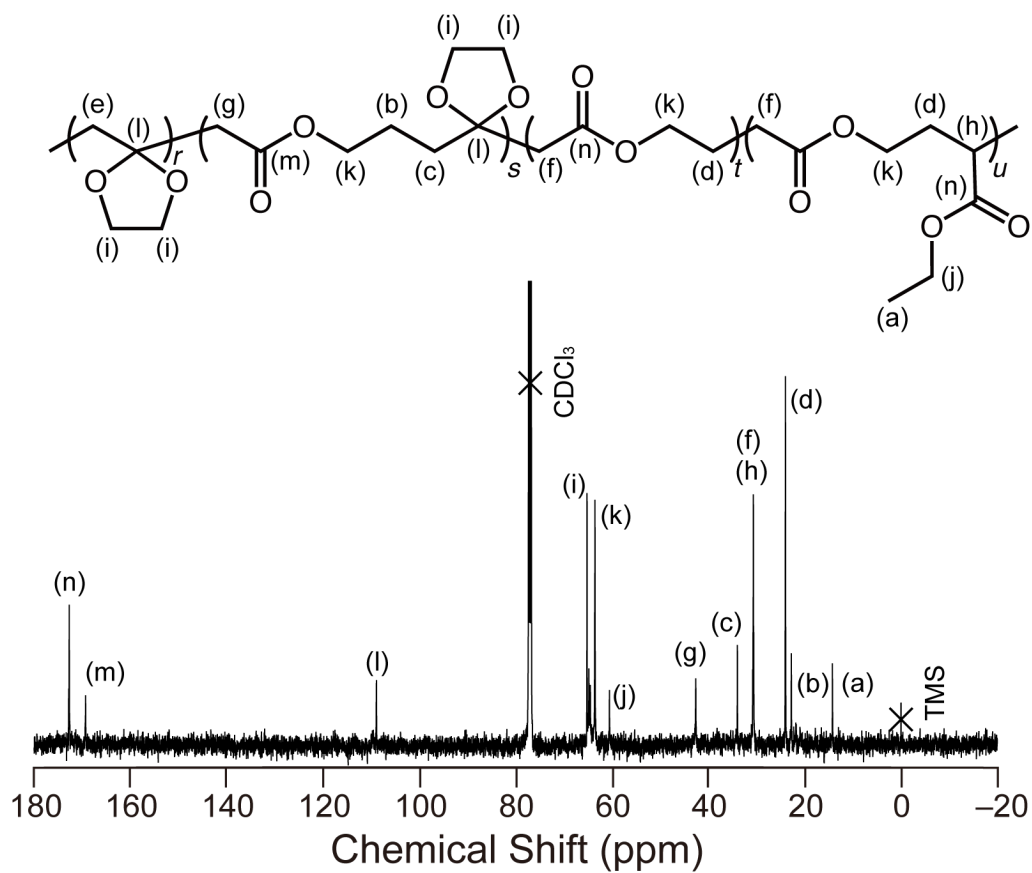


Figure S3. ^{13}C NMR spectrum of the polymer obtained by polymerization of **C5** at 120 °C. The spectrum was measured in CDCl_3 at 25 °C.

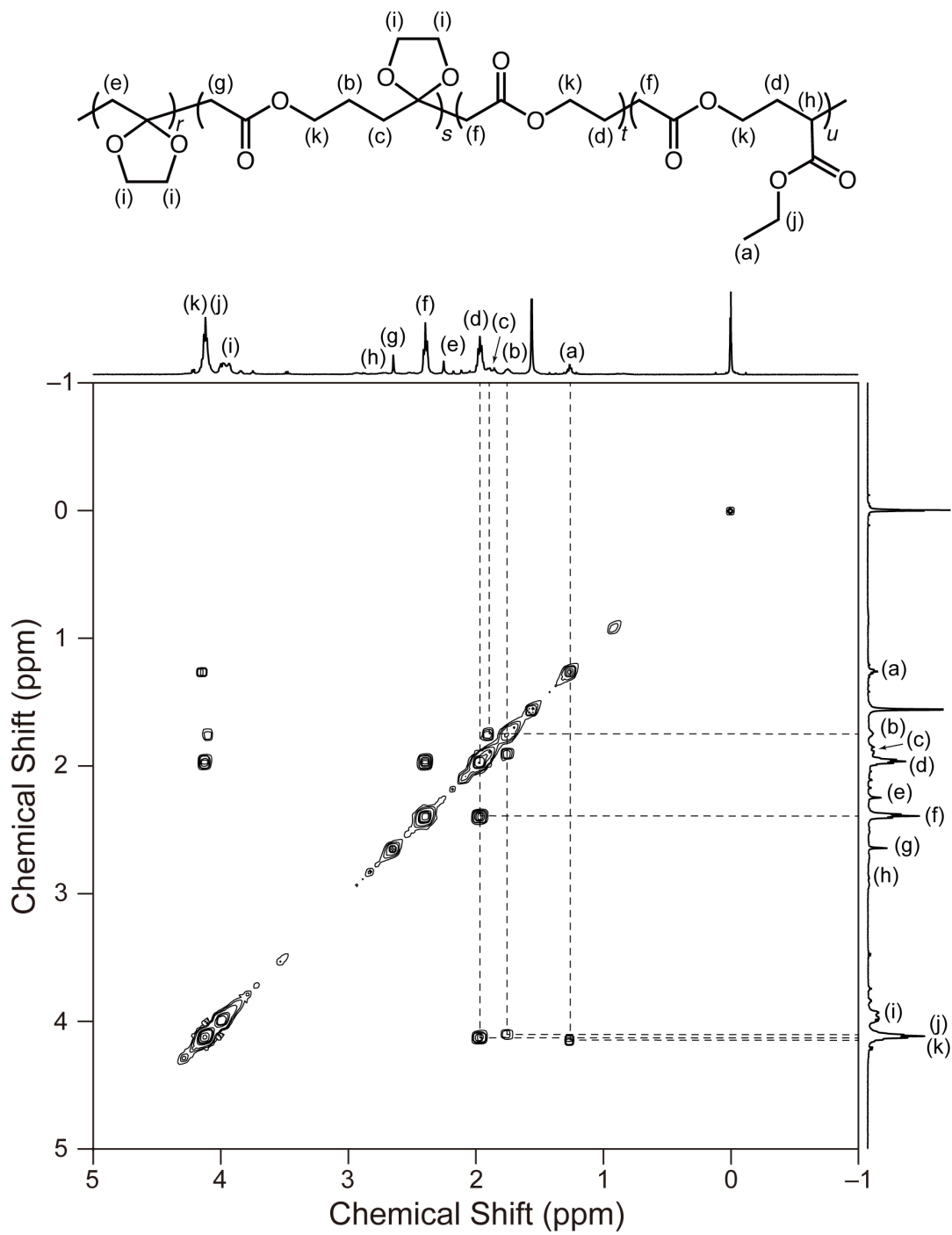


Figure S4. H-H COSY spectrum of the polymer obtained by polymerization of **C5** at 120 °C. The spectrum was measured in CDCl₃ at 25 °C.

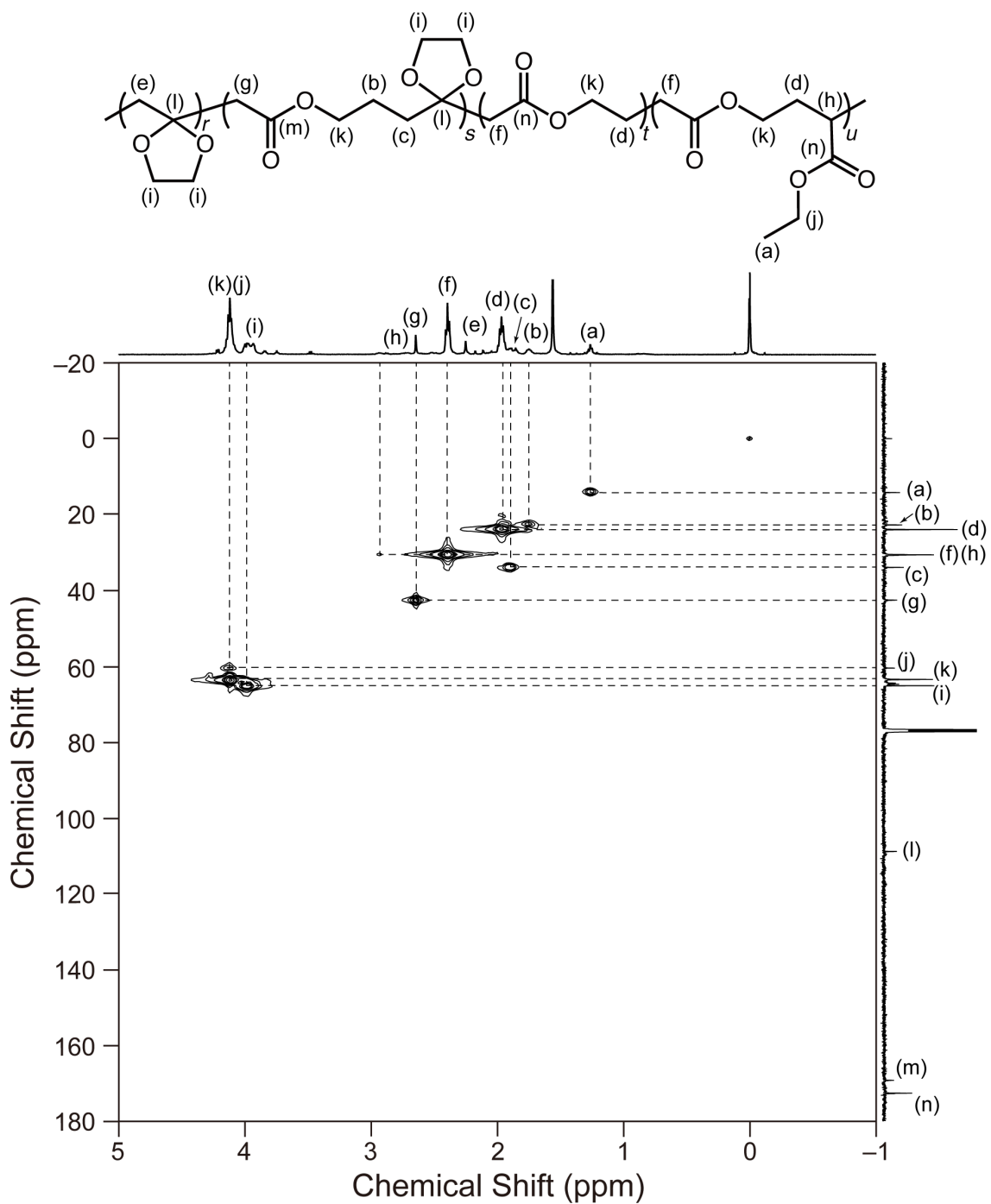


Figure S5. HMBC spectrum of the polymer obtained by polymerization of **C5** at 120 °C. The spectrum was measured in CDCl_3 at 25 °C.

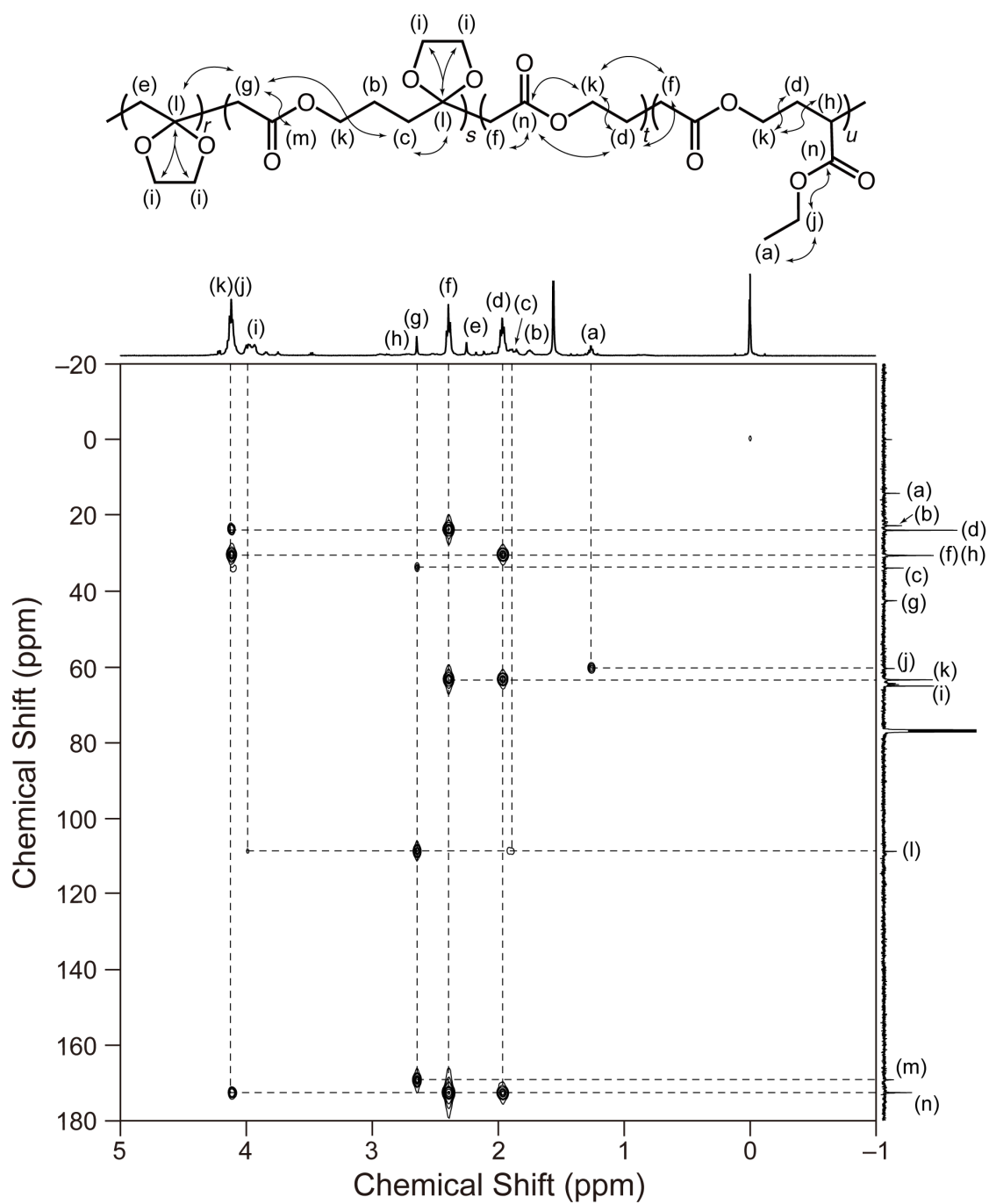
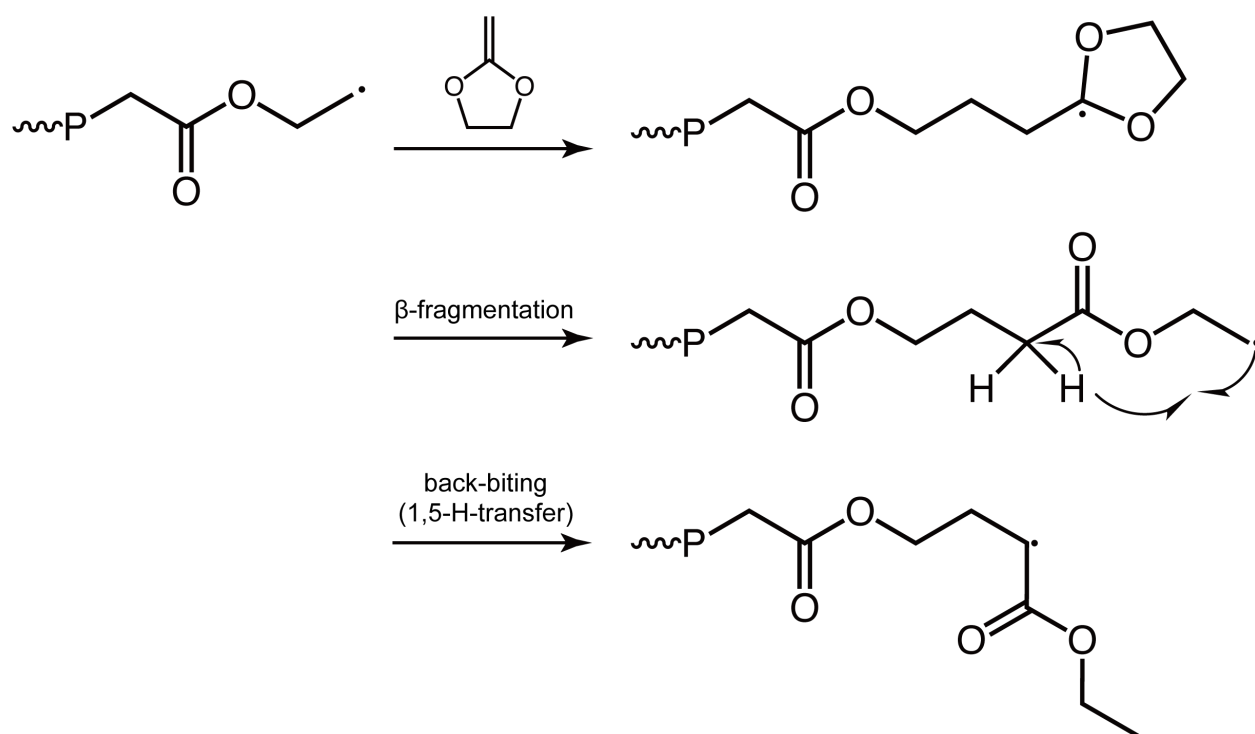
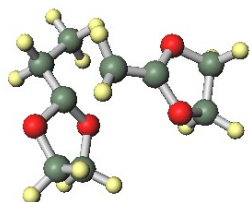
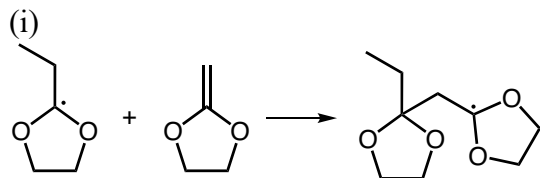


Figure S6. HMBC spectrum of the polymer obtained by polymerization of **C5** at 120 °C. The spectrum was measured in CDCl_3 at 25 °C.



Scheme S1. Mechanism of back-biting (1,5-H-transfer) reaction that occurred during the propagation reaction of C5 polymerization.

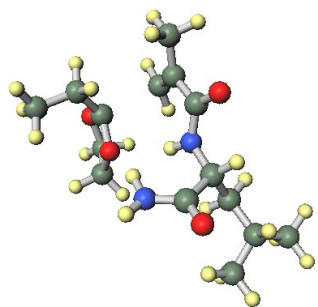
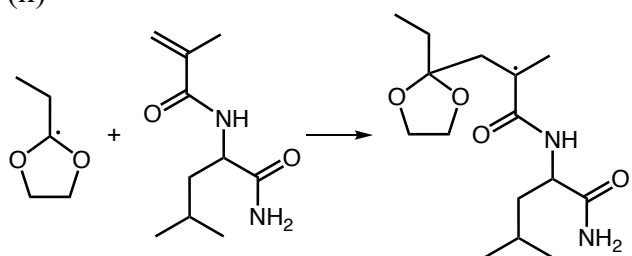
The 3D Structures and Cartesian Coordinates for The Transition States in The Reactions



	x	y	z
C	-0.0554	2.295652	-0.932439
C	-0.316337	1.37979	0.268216
C	0.763052	0.352759	0.480132
C	2.691086	1.394078	1.101902
C	3.569172	1.386735	0.059745
O	3.586895	2.343754	-0.927982
C	4.528963	1.923346	-1.919703
C	4.585486	0.412579	-1.696215
O	4.352995	0.311642	-0.284585
O	0.48032	-0.533964	1.515707
C	1.239351	-1.710565	1.248652
C	1.257897	-1.759009	-0.284007
O	1.094978	-0.389187	-0.661579
H	-0.847569	3.047189	-1.020037
H	0.904463	2.813235	-0.842954
H	-0.032406	1.71523	-1.860141
H	-0.404719	1.967289	1.190308
H	-1.28023	0.858957	0.136173
H	2.256577	2.345582	1.386162
H	2.844336	0.675041	1.897425
H	4.154195	2.215821	-2.903273

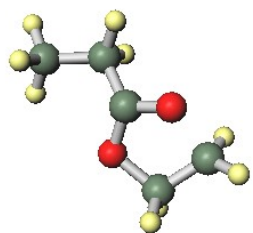
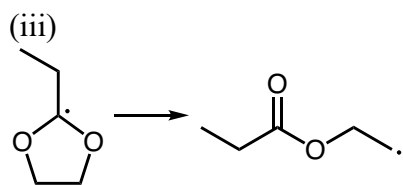
H	5.500774	2.401347	-1.737563
H	3.784676	-0.104876	-2.239787
H	5.551863	-0.041863	-1.92395
H	2.254734	-1.614878	1.656119
H	0.736696	-2.559723	1.717612
H	2.200569	-2.140732	-0.688085
H	0.425594	-2.349163	-0.689554

(ii)



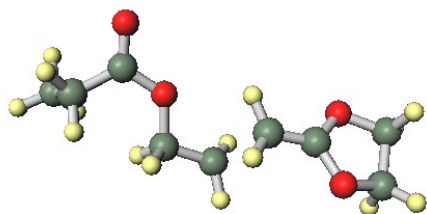
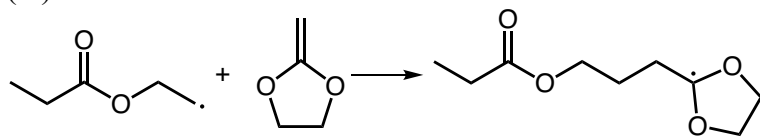
	x	y	z
C	1.249716	3.442901	-1.313382
C	1.872197	2.092018	-1.546832
C	1.136496	0.939	-1.58041
C	1.139745	-0.15982	0.514874
O	2.417605	-0.735908	0.598609
C	2.270424	-2.169756	0.595558
C	0.873799	-2.353097	0.003439
O	0.20059	-1.16602	0.43747
C	0.839145	0.915106	1.519775
C	0.849635	0.419319	2.976826
C	3.353241	2.108979	-1.735986
N	4.009408	0.91215	-1.542399
C	5.450015	0.771153	-1.693446
C	5.761185	-0.452895	-2.591865
C	7.250659	-0.701276	-2.947674
C	7.376443	-1.169234	-4.40663
C	7.9182	-1.714597	-2.004255
C	6.210357	0.731153	-0.353974

N	5.505122	0.300854	0.736465
O	7.402269	1.00581	-0.297346
O	3.950416	3.14225	-2.038097
H	1.497435	4.119874	-2.138396
H	0.161185	3.369251	-1.227966
H	1.640152	3.920286	-0.405134
H	0.051079	0.9846	-1.560869
H	1.551924	0.021471	-1.986889
H	3.073394	-2.60632	-0.0025
H	2.334626	-2.542193	1.62488
H	0.893628	-2.396188	-1.093047
H	0.331651	-3.216186	0.394107
H	1.57362	1.715774	1.381747
H	-0.139921	1.338077	1.269146
H	0.627684	1.242571	3.664113
H	0.099192	-0.363054	3.129284
H	1.830898	0.012472	3.244631
H	3.483225	0.129979	-1.177201
H	5.793212	1.680319	-2.192065
H	5.339444	-1.356487	-2.124546
H	5.184827	-0.288752	-3.510585
H	7.78666	0.250107	-2.844537
H	8.424744	-1.347098	-4.674615
H	6.830121	-2.108351	-4.568725
H	6.973165	-0.424667	-5.103359
H	8.972012	-1.856357	-2.27273
H	7.886321	-1.380419	-0.964379
H	7.424603	-2.694104	-2.073399
H	5.980634	0.363331	1.626639
H	4.494289	0.280886	0.743732



	x	y	z
C	3.581202	-0.922577	-0.566127
C	2.326317	-0.160008	-0.12432
C	1.041309	-0.795902	-0.59197
O	0.889575	-2.11389	-0.29544
C	-0.523392	-2.371323	0.032484
C	-1.170166	-1.063009	0.35022
O	-0.057206	-0.150592	-0.742839
H	4.483604	-0.433512	-0.184653
H	3.563544	-1.95033	-0.191139
H	3.6513	-0.964255	-1.658565
H	2.304716	-0.096321	0.978795
H	2.339754	0.867937	-0.500012
H	-0.986769	-2.855308	-0.832927
H	-0.49505	-3.069818	0.872099
H	-2.137041	-0.839953	-0.085347
H	-1.009928	-0.649245	1.342922

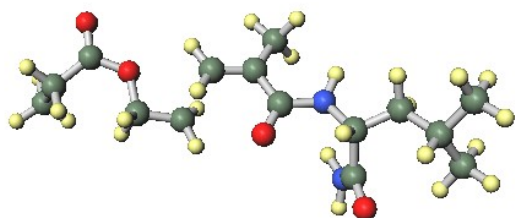
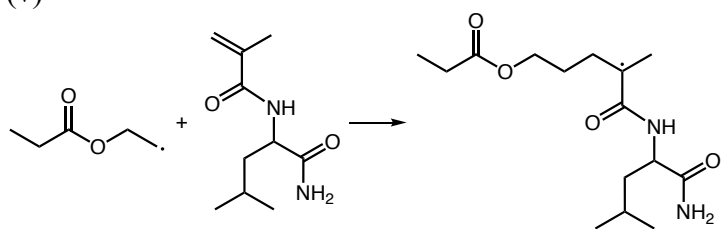
(iv)



	x	y	z
O	1.905661	5.683475	-2.147622
C	1.843254	5.461999	-0.960011
O	1.374152	4.255736	-0.549226
C	1.285941	3.890673	0.849742
C	0.601742	2.570843	0.943619
C	1.849814	1.117867	-0.399373
C	1.244915	-0.09305	-0.471874
O	0.206545	-0.382613	-1.312388
C	-0.073638	-1.782116	-1.183653
C	0.433601	-2.085647	0.225896
O	1.498078	-1.136521	0.377182
C	2.223719	6.516063	0.073681
C	1.049183	7.479048	0.330572
H	2.295166	3.840815	1.282067
H	0.73587	4.682949	1.386036
H	0.685177	2.057828	1.898085
H	-0.361335	2.484307	0.447724
H	1.73944	1.808557	-1.223537
H	2.721606	1.209152	0.23576
H	-1.146466	-1.934136	-1.317585
H	0.478016	-2.342745	-1.949361
H	-0.335199	-1.903839	0.988067

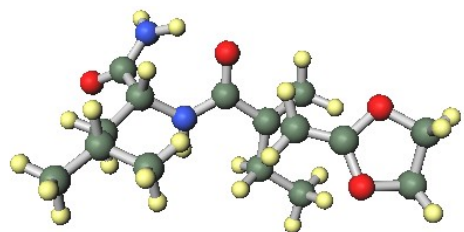
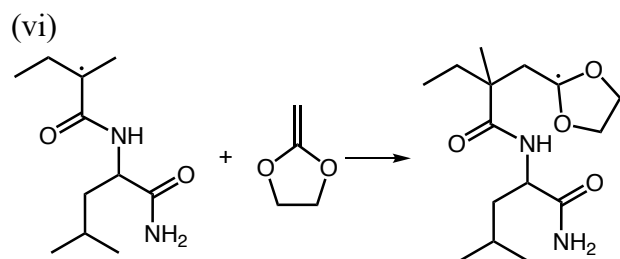
H	0.843688	-3.090072	0.34923
H	2.568241	6.075831	1.013782
H	3.059067	7.072611	-0.360424
H	1.353779	8.281122	1.0107
H	0.718597	7.929939	-0.610095
H	0.192452	6.963116	0.77856

(v)



	x	y	z
O	5.247564	1.709123	-1.283173
C	4.525537	0.814371	-0.912492
O	3.274771	1.136466	-0.476106
C	2.327756	0.140318	-0.037074
C	1.140577	0.847675	0.511167
C	0.295572	2.100244	-1.41146
C	-0.699777	2.912846	-0.973577
C	-0.451937	4.344413	-0.565823
C	-2.061082	2.305995	-0.853057
N	-3.088715	3.163978	-0.510519
C	-4.481317	2.716364	-0.58813
C	-5.391057	3.961942	-0.683234
C	-6.910179	3.691895	-0.838533
C	-7.538138	4.730466	-1.781868
C	-7.64558	3.685113	0.51122
C	-4.871764	1.787617	0.576133
N	-4.210164	2.003899	1.753057
O	-5.781542	0.980237	0.456683
O	-2.274132	1.104056	-1.008721
C	4.987244	-0.6362	-0.867635

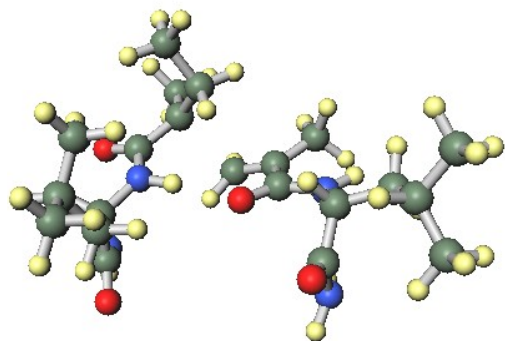
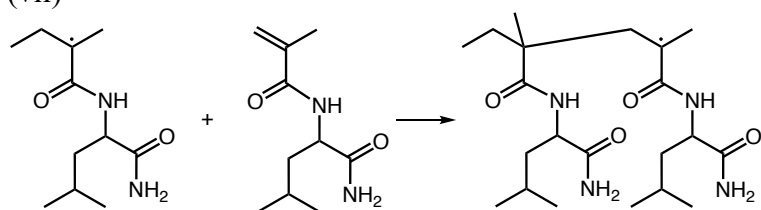
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H	2.797959	-0.497947	0.7302
H	0.214624	0.29366	0.620005
H	1.314044	1.675672	1.191086
H	1.300228	2.472676	-1.580073
H	0.043876	1.11959	-1.798868
H	-0.783855	4.54677	0.461766
H	0.61365	4.58323	-0.624279
H	-0.976255	5.057192	-1.219713
H	-2.926809	4.159099	-0.589584
H	-4.610554	2.100865	-1.484649
H	-5.216466	4.601089	0.19454
H	-5.037241	4.527921	-1.556586
H	-7.032341	2.699217	-1.289737
H	-8.61349	4.554039	-1.900488
H	-7.411765	5.74828	-1.388742
H	-7.080878	4.698114	-2.77838
H	-8.712779	3.481005	0.364928
H	-7.253772	2.918715	1.183973
H	-7.55932	4.662064	1.006083
H	-4.356631	1.319753	2.483106
H	-3.319703	2.480043	1.728049
H	4.159696	-1.342561	-0.979389
H	5.652319	-0.764986	-1.726019
H	6.164561	-1.943502	0.416624
H	6.606658	-0.227373	0.526908
H	5.135248	-0.818159	1.317806



	x	y	z
O	1.061697	-4.83758	-0.639262
C	1.793923	-3.925119	-1.075662
N	3.12004	-4.170102	-1.335164
C	3.749972	-5.4822	-1.150783
C	5.265156	-5.350606	-0.933222
C	5.720559	-5.167313	0.527553
C	5.187457	-3.885374	1.184228
C	7.254204	-5.215455	0.606521
C	3.434147	-6.402894	-2.366248
N	2.136606	-6.807031	-2.410236
O	4.280822	-6.731195	-3.188344
C	1.297607	-2.537878	-1.245877
C	2.220323	-1.535787	-1.92677
C	1.694229	-0.099337	-2.043602
C	-0.171535	-2.461636	-1.591984
C	1.311348	-2.066115	0.872292
C	0.558432	-0.984281	1.265195
O	-0.792941	-1.027396	1.449069
C	-1.197928	0.24894	1.965041
C	-0.101444	1.17554	1.439758

O	1.032198	0.29547	1.361081
H	3.655332	-3.484298	-1.847179
H	3.273127	-5.926338	-0.269611
H	5.731465	-6.251199	-1.343921
H	5.652774	-4.524321	-1.54859
H	5.329993	-6.022901	1.10037
H	5.549062	-3.798932	2.216072
H	5.529144	-2.994561	0.639279
H	4.093795	-3.86341	1.208878
H	7.599475	-5.139684	1.644386
H	7.648023	-6.148336	0.186548
H	7.701627	-4.383789	0.046466
H	1.827808	-7.298497	-3.238031
H	1.456304	-6.366006	-1.792051
H	3.18506	-1.502583	-1.400982
H	2.44319	-1.895838	-2.947862
H	2.428309	0.527478	-2.562062
H	0.761404	-0.054944	-2.61511
H	1.51841	0.339328	-1.05728
H	-0.612569	-1.504631	-1.297308
H	-0.326558	-2.573751	-2.677371
H	-0.716861	-3.264937	-1.093028
H	0.907039	-3.040215	1.123304
H	2.38678	-1.947252	0.949764
H	-2.196086	0.473829	1.585253
H	-1.217247	0.211564	3.061438
H	-0.330915	1.564247	0.43997
H	0.147814	2.000947	2.109086

(vii)



	x	y	z
O	5.254781	3.443728	1.949904
C	4.142237	3.331262	1.403371
N	3.864048	2.353747	0.50058
C	4.838211	1.338172	0.086241
C	4.498203	0.779092	-1.304713
C	5.15315	1.507952	-2.49411
C	4.740396	2.982056	-2.613546
C	4.848333	0.755471	-3.798338
C	4.958359	0.191673	1.140364
N	5.246427	0.630984	2.397549
O	4.8154	-0.990913	0.862264
C	3.035977	4.289964	1.737845
C	2.221446	4.872034	0.600622
C	3.000374	5.925323	-0.214487
C	3.356486	5.222674	2.877725
C	1.628634	2.822476	2.754281
C	0.361353	2.892989	2.215039
C	-0.716162	3.760387	2.817661

C	0.098082	2.129383	0.971442
N	-1.214146	1.925722	0.626493
C	-1.589415	1.392658	-0.68511
C	-3.077606	1.727521	-0.934973
C	-3.652027	1.312508	-2.314644
C	-4.628369	2.384597	-2.824345
C	-4.341297	-0.060504	-2.27022
C	-1.280405	-0.108212	-0.846058
N	-1.308538	-0.854423	0.29887
O	-1.115178	-0.588057	-1.957523
O	1.002039	1.669744	0.254676
H	2.884798	2.160343	0.281448
H	5.815639	1.837414	0.069445
H	4.808289	-0.270042	-1.312397
H	3.406291	0.766409	-1.431644
H	6.243161	1.477126	-2.337552
H	5.219547	3.450973	-3.481763
H	3.653924	3.07465	-2.742166
H	5.021277	3.55726	-1.725501
H	5.349687	1.225143	-4.653082
H	5.179218	-0.288249	-3.744238
H	3.770301	0.751883	-4.005264
H	5.440502	-0.069082	3.100159
H	5.511302	1.602092	2.550677
H	1.885168	4.080549	-0.074707
H	1.319632	5.34182	1.013826
H	2.372722	6.313234	-1.024746
H	3.306556	6.772994	0.407347
H	3.899713	5.493419	-0.665361
H	2.458534	5.75368	3.213957
H	3.804392	4.690457	3.720515
H	4.092473	5.976463	2.563944

H	2.276721	2.000876	2.475443
H	1.806549	3.260388	3.731511
H	-1.549086	3.163141	3.219891
H	-0.319814	4.345794	3.652048
H	-1.145683	4.464011	2.09126
H	-1.937096	2.37882	1.167928
H	-0.975005	1.879508	-1.449649
H	-3.68411	1.281122	-0.13327
H	-3.164103	2.81739	-0.822039
H	-2.816493	1.242683	-3.02205
H	-5.043902	2.1048	-3.799107
H	-5.470217	2.51367	-2.130958
H	-4.135582	3.358073	-2.936793
H	-4.721597	-0.33081	-3.262141
H	-3.654157	-0.849416	-1.955673
H	-5.19542	-0.045046	-1.579675
H	-0.963104	-1.802084	0.21832
H	-1.171766	-0.391771	1.186251