Supporting Information for "New Mechanism for Autoxidation of polyolefins: kinetic Monte Carlo Modelling of the Role of Short-chain Branches, Molecular Oxygen and Unsaturated Moieties"

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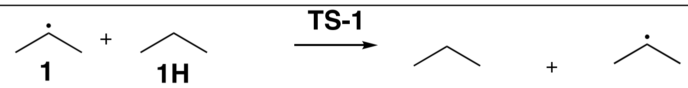
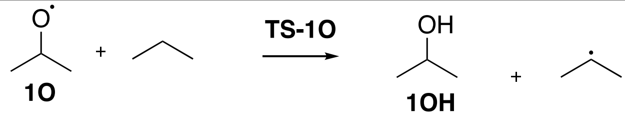
S1. Details of computational framework

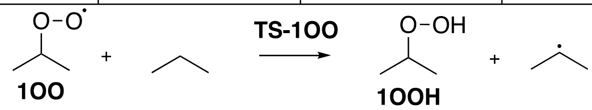
Table S1. Energetics of the hydrogen abstraction calculations: ZPVE-corrected energies, enthalpies and Gibbs free energies in the gas phase at 298K; Calculations performed at the G3(MP2)CC// M062X/6-31+G(d,p) level of theory.



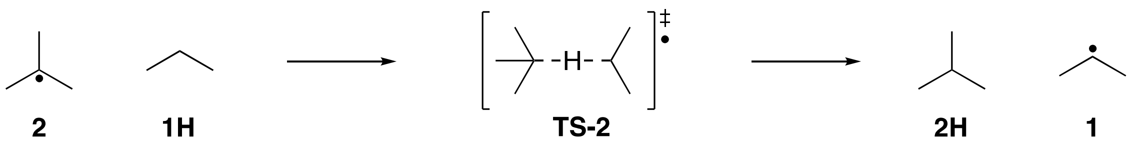
ΔG (kJ mol^{-1})	$\Delta G^{\ddagger}_{f}$ (kJ mol^{-1})	$\Delta G^{\ddagger}_{r}$ (kJ mol^{-1})	$\kappa(T)$	k_f (L mol^{-1} s^{-1})	k_r (L mol^{-1} s^{-1})
0.0	103.4	103.4	3.8E+01	1.2E-04	1.2E-04
ΔH	$\Delta H^{\ddagger}_{f}$	$\Delta H^{\ddagger}_{r}$	ΔE	$\Delta E^{\ddagger}_{f}$	$\Delta E^{\ddagger}_{r}$
0.0	52.3	52.3	0.0	61.0	61.0



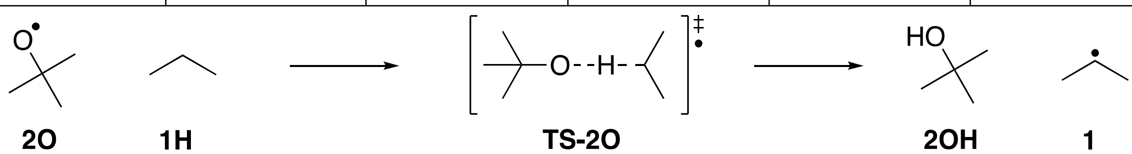
ΔG	$\Delta G^{\ddagger}_{f}$	$\Delta G^{\ddagger}_{r}$	$\kappa(T)$	k_f	k_r
-37.8	66.2	104.0	5.8E+00	3.8E+02	9.2E-05
ΔH	$\Delta H^{\ddagger}_{f}$	$\Delta H^{\ddagger}_{r}$	ΔE	$\Delta E^{\ddagger}_{f}$	$\Delta E^{\ddagger}_{r}$
-32.6	18.0	50.6	-31.2	26.8	58.0



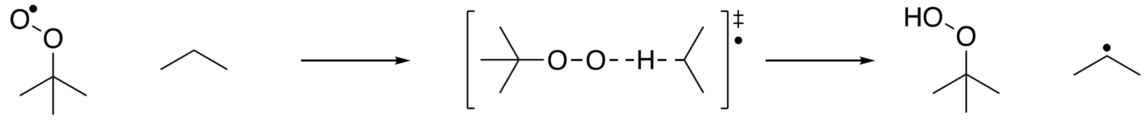
ΔG	$\Delta G^{\ddagger}_{f}$	$\Delta G^{\ddagger}_{r}$	$\kappa(T)$	k_f	k_r
50.1	124.2	74.0	3.2E+02	2.7E-08	1.6E+01
ΔH	$\Delta H^{\ddagger}_{f}$	$\Delta H^{\ddagger}_{r}$	ΔE	$\Delta E^{\ddagger}_{f}$	$\Delta E^{\ddagger}_{r}$
56.3	74.2	17.9	62.8	88.3	25.6



ΔG	$\Delta G^{\ddagger}_{f}$	$\Delta G^{\ddagger}_{r}$	$\kappa(T)$	k_f	k_r
1.90	97.00	95.10	1.18×10^{1}	1.82×10^{-2}	3.92×10^{-2}
ΔH	$\Delta H^{\ddagger}_{f}$	$\Delta H^{\ddagger}_{r}$	ΔE	$\Delta E^{\ddagger}_{f}$	$\Delta E^{\ddagger}_{r}$
4.20	54.57	50.37	5.57	62.07	56.50

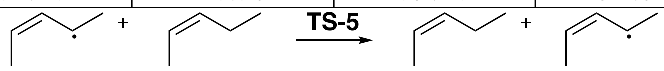


ΔG	$\Delta G^{\ddagger}_{f}$	$\Delta G^{\ddagger}_{r}$	$\kappa(T)$	k_f	k_r
-41.80	70.87	112.67	6.57×10^{0}	3.84×10^{2}	1.82×10^{-5}
ΔH	$\Delta H^{\ddagger}_{f}$	$\Delta H^{\ddagger}_{r}$	ΔE	$\Delta E^{\ddagger}_{f}$	$\Delta E^{\ddagger}_{r}$
-36.88	25.17	62.05	-33.49	33.20	66.69



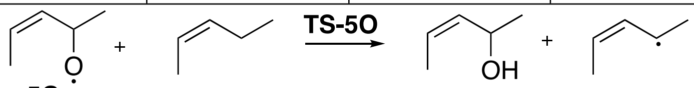
2OO 1H TS-2OO 2OOH 1

ΔG	$\Delta G^‡_f$	$\Delta G^‡_r$	$\kappa(T)$	k_f	k_r
47.13	126.15	79.02	3.30×10^{1}	3.97×10^{-7}	7.18×10^{1}
ΔH	$\Delta H^‡_f$	$\Delta H^‡_r$	ΔE	$\Delta E^‡_f$	$\Delta E^‡_r$
53.03	81.40	28.37	59.10	92.74	33.64



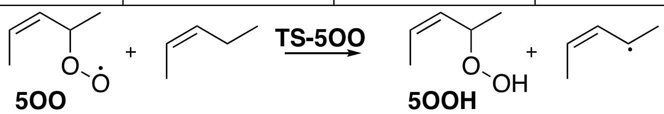
5 5H

ΔG	$\Delta G^‡_f$	$\Delta G^‡_r$	$\kappa(T)$	k_f	k_r
0.0	109.6	109.6	5.2E+01	9.6E-06	9.6E-06
ΔH	$\Delta H^‡_f$	$\Delta H^‡_r$	ΔE	$\Delta E^‡_f$	$\Delta E^‡_r$
0.0	68.7	68.7	0.0	74.0	74.0



5O 5OH

ΔG	$\Delta G^‡_f$	$\Delta G^‡_r$	$\kappa(T)$	k_f	k_r
-97.0	49.3	146.3	2.4E+00	3.4E+05	3.5E-12
ΔH	$\Delta H^‡_f$	$\Delta H^‡_r$	ΔE	$\Delta E^‡_f$	$\Delta E^‡_r$
-95.6	0.3	95.9	-96.8	7.4	104.2



5OO 5OOH

ΔG	$\Delta G^‡_f$	$\Delta G^‡_r$	$\kappa(T)$	k_f	k_r
-16.6	86.9	103.5	8.0E+02	9.0E-02	1.1E-04
ΔH	$\Delta H^‡_f$	$\Delta H^‡_r$	ΔE	$\Delta E^‡_f$	$\Delta E^‡_r$
-15.5	35.6	51.0	-14.1	45.2	59.4

Table S2. Raw computational data: entropies (J mol^{-1} K^{-1}), thermal corrections and total energies (in Hartrees, 298.15 K); related to Table S1.

Species	*Entropy (S^{298})* **(J mol^{-1} K^{-1})**	*TC^{298}*	*ZPVE*	*HLC*	*SO*	*M06-2X*	*MP2/small*	*MP2/large*	*URCCSD(T)*	*E_0*	*H^{298}*	*G^{298}*
1	277.427	0.09	0.09	-0.09	0.00	-118.41	-118.01	-118.17	-118.06	-118.31	-118.14	-118.17
1H	258.704	0.10	0.10	-0.10	0.00	-119.08	-118.66	-118.83	-118.72	-118.99	-118.79	-118.82
1O	299.35	0.01	0.09	-0.12	0.00	-193.60	-193.03	-193.27	-193.10	-193.45	-193.35	-193.39
1OH	296.91	0.01	0.11	-0.12	0.00	-194.27	-193.69	-193.95	-193.75	-194.14	-194.02	-194.06
1OO	325.09	0.01	0.10	-0.15	0.00	-268.74	-268.00	-268.33	-268.08	-268.55	-268.44	-268.48
1OOH	325.98	0.01	0.11	-0.15	0.00	-269.38	-268.63	-268.97	-268.70	-269.19	-269.07	-269.11
TS-1	396.42	0.01	0.19	-0.18	0.00	-237.46	-236.64	-236.99	-236.75	-237.28	-237.07	-237.12
TS-1O	411.71	0.01	0.20	-0.21	0.00	-312.67	-311.67	-312.09	-311.79	-312.43	-312.22	-312.27
TS-1OO	431.49	0.01	0.20	-0.24	0.00	-387.78	-386.63	-387.14	-386.76	-387.50	-387.29	-387.34
2	295.48	0.12	0.11	-0.12	0.00	-157.71	-157.18	-157.39	-157.25	-157.58	-157.35	-157.38
2H	284.49	0.13	0.13	-0.13	0.00	-158.37	-157.84	-158.06	-157.90	-158.25	-157.99	-158.03
2O	306.24	0.12	0.12	-0.15	0.00	-232.90	-232.21	-232.49	-232.29	-232.72	-232.48	-232.51
2OH	304.01	0.14	0.13	-0.16	0.00	-233.58	-232.88	-233.18	-232.95	-233.41	-233.14	-233.17
2OO	328.19	0.13	0.12	-0.18	0.00	-308.04	-307.19	-307.55	-307.28	-307.81	-307.56	-307.60
2OOH	329.24	0.14	0.14	-0.19	0.00	-308.68	-307.83	-308.20	-307.90	-308.46	-308.19	-308.22
TS-2	411.87	0.22	0.21	-0.22	0.00	-276.77	-275.83	-276.21	-275.94	-276.54	-276.12	-276.16
TS-2O	411.67	0.22	0.22	-0.25	0.00	-351.97	-350.86	-351.32	-350.99	-351.69	-351.26	-351.30
TS-2OO	436.78	0.23	0.22	-0.28	0.00	-427.09	-425.83	-426.36	-425.96	-426.76	-426.32	-426.37
5	335.85	0.01	0.12	-0.14	0.00	-195.80	-195.16	-195.41	-195.24	-195.63	-195.50	-195.54
5H	330.98	0.01	0.14	-0.14	0.00	-196.44	-195.79	-196.05	-195.87	-196.27	-196.13	-196.17
5O	355.56	0.01	0.13	-0.16	0.00	-270.96	-270.16	-270.48	-270.25	-270.74	-270.61	-270.65
5OH	355.41	0.01	0.14	-0.17	0.00	-271.64	-270.82	-271.17	-270.90	-271.42	-271.27	-271.31
5OO	381.99	0.01	0.13	-0.19	0.00	-346.10	-345.13	-345.54	-345.23	-345.84	-345.69	-345.74
5OOH	380.89	0.01	0.15	-0.20	0.00	-346.74	-345.76	-346.19	-345.86	-346.48	-346.33	-346.37
TS-5	529.74	0.02	0.26	-0.28	0.00	-392.21	-390.92	-391.44	-391.08	-391.87	-391.60	-391.66
TS-5O	522.16	0.02	0.26	-0.31	0.00	-467.40	-465.93	-466.53	-466.11	-467.01	-466.73	-466.79
TS-5OO	540.74	0.02	0.27	-0.33	0.00	-542.52	-540.90	-541.58	-541.08	-542.09	-541.81	-541.87

Table S3. Gaussian archive entries.

i-propyl

```
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 .\Quadrupole=-0.4683822,0.1796789,0.2887032,-0.3569512,0.,0.\PG=CS [SG
 (C1H1),X(C2H6)]\\@

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 X(C2H6)]\\@

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TS-1.a1
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 ,2.0233958573,1.5114528177\H,3.0231447824,2.3300984525,-0.6508932209\H
 ,3.5692580895,-0.5115993623,0.4333811445\H,4.8294406735,0.4933251182,-
 0.290469932\H,3.471185868,-0.0653046148,-1.2788281844\H,2.9265308122,1
 .2397956186,2.2362825194\H,2.5654511014,2.9009864588,1.7348217868\H,4.
 2293027256,2.297939672,1.6868155847\H,1.6703693681,1.1633791389,0.0374
 515482\\Version=ES64L-G09RevE.01\State=2-A\HF=-237.4647076\S2=0.758678
 \S2-1=0.\S2A=0.750041\RMSD=8.118e-09\RMSF=2.714e-06\Dipole=-0.0031753,
 0.0096079,-0.0207877\Quadrupole=-0.0287363,-0.0340585,0.0627947,0.1281
 328,0.0817363,-0.0895912\PG=C01 [X(C6H15)]\\@

TS-1O.a1c3
 1\1\GINC-R123\FTS\UM062X\6-31+G(d,p)\C6H15O1(2)\ROOT\05-Sep-2017\0\\#M
 062X/6-31+G** SCF=Tight IOP(2/17=4) INT(grid=ultrafine) OPT(TS,calcfc,
 noeigentest,maxcyc=200) maxdisk=671088640\\a1 b1 c3\\0,2\C,-1.88926663
 25,-1.5984081729,0.7828466338\C,-1.9485588943,-1.6381988837,-0.7407519
 942\C,-2.7671916613,-0.4808523129,1.3549557179\H,-2.2448083202,-2.5574
 229205,1.1960852219\H,-1.6087562177,-0.6811031235,-1.1485009483\H,-2.9
 687342667,-1.829241714,-1.0885465115\H,-1.2988214449,-2.4264557092,-1.
 1343524159\H,-2.4297976532,0.4870542185,0.9735172713\H,-2.7084750394,-
```

```
0.4685872039,2.4451789807\H,-3.807318705,-0.6371503387,1.0541297634\O,
-0.594165846,-1.3281418556,1.2509164693\C,0.7880729087,-3.3741904251,0
.6845605011\C,-0.1539188929,-4.534832651,0.9262887387\C,1.9561588921,-
3.2924130315,1.6459861762\H,1.0989225798,-3.2942133396,-0.3626981705\H
,-0.5461879086,-4.508459513,1.9486034973\H,0.3723538244,-5.4894058381,
0.7980681154\H,-1.0006432704,-4.528666944,0.232849864\H,1.6008935673,-
3.2588343006,2.6805847999\H,2.5626432657,-2.401744239,1.464688109\H,2.
6038205559,-4.1723170707,1.5410074391\H,0.161375159,-2.351765631,0.880
1497415\\Version=ES64L-G09RevE.01\State=2-A\HF=-312.6659354\S2=0.75881
4\S2-1=0.\S2A=0.750037\RMSD=6.311e-09\RMSF=4.241e-06\Dipole=-0.2350802
,-0.5463077,-0.2711747\Quadrupole=1.7334593,-0.8312014,-0.9022579,-1.9
174141,-0.2455096,-0.5935546\PG=C01 [X(C6H15O1)]\\@
```

TS-1OO.a1c3

```
1\1\GINC-R3091\FTS\UM062X\6-31+G(d,p)\C6H15O2(2)\ROOT\05-Sep-2017\0\\#
M062X/6-31+G** SCF=Tight IOP(2/17=4) INT(grid=ultrafine) OPT(TS,calcfc
,noeigentest,maxcyc=200) maxdisk=1073741824\\a1 b1 c3\\0,2\C,-0.631643
3996,-0.6803578791,0.0968256692\C,0.4205054823,-0.5647047554,-0.992187
0478\C,-0.0378696335,-0.8879918448,1.4804092056\H,-1.2867800527,0.2020
436427,0.094858604\H,1.0265877104,-1.4748314885,-1.0264509747\H,1.0792
187246,0.2826506953,-0.7846494935\H,-0.0418839946,-0.4177250091,-1.971
7399312\H,0.6174061301,-1.7645689894,1.4773865722\H,-0.8317566283,-1.0
443457966,2.2133599168\H,0.5479151213,-0.0127117273,1.7764549741\O,-1.
4321666163,-1.8109167892,-0.2804070202\O,-2.5361870453,-1.8841221543,0
.5548733304\C,-4.2443601973,-1.0124446311,-1.0634150136\C,-4.332896081
5,-2.2219010736,-1.9591264597\C,-3.5832340985,0.2022061155,-1.66372152
82\H,-5.1522764929,-0.7982447835,-0.492498746\H,-3.3357515459,-2.50625
74037,-2.3118831609\H,-4.951021782,-2.0047571954,-2.8415908313\H,-4.77
09318903,-3.0780302827,-1.4408944176\H,-2.5808223812,-0.0499531712,-2.
028677115\H,-3.5013779442,1.0229518772,-0.9461085739\H,-4.1608448246,0
.5657200734,-2.5253980468\H,-3.41279956,-1.4230564292,-0.1140229119\\V
ersion=ES64L-G09RevE.01\State=2-A\HF=-387.7842911\S2=0.759691\S2-1=0.\
S2A=0.750047\RMSD=6.554e-09\RMSF=6.162e-07\Dipole=-0.0235078,0.7906988
,-0.3910532\Quadrupole=3.2921846,-1.9572434,-1.3349412,0.6119291,1.586
9407,0.9629497\PG=C01 [X(C6H15O2)]\\@
```

t-butyl

2.M062X

```
1\1\GINC-N0919\FOpt\UM062X\6-31+G(d,p)\C4H9(2)\HD_IL182\19-Apr-2021\0\
\#UM062X/6-31+G(d,p) SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) Nos
ymm\\2.m062x.freq\\0,2\C,0.,0.,0.1097135059\C,0.7401406193,-1.28196294
33,-0.0976400468\C,0.740142166,1.2819620504,-0.0976400468\C,-1.4802827
853,0.0000008929,-0.0976400468\H,1.7431805951,-1.2436847725,0.33984589
\H,0.8687498172,-1.5047209186,-1.1715729011\H,0.2054697383,-2.13148131
29,0.33984589\H,1.7431820955,1.2436826695,0.33984589\H,0.2054723098,2.
131481065,0.33984589\H,0.8687516325,1.5047198705,-1.1715729011\H,-1.73
75014497,0.0000010481,-1.1715729011\H,-1.9486518338,0.8877986434,0.339
84589\H,-1.9486529048,-0.8877962924,0.33984589\\Version=ES64L-G16RevC.
01\HF=-157.712128\S2=0.754946\S2-1=0.\S2A=0.75002\RMSD=4.419e-09\RMSF=
4.239e-06\Dipole=0.0000069,0.,-0.1184819\Quadrupole=0.2520073,0.251937
2,-0.5039446,0.,-0.0000224,0.\PG=C03V [C3(C1),3SGV(C1H1),X(H6)]\\@
```

2H.M062X

```
1\1\GINC-N1009\FOpt\RM062X\6-31+G(d,p)\C4H10\HD_IL182\19-Apr-2021\0\\#
M062X/6-31+G(d,p) SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) Nosymm
\\2h.m062x.freq\\0,1\C,0.0000707654,0.0000924373,0.3829399251\C,0.7262
801919,-1.2578485825,-0.0947350502\C,0.7262866314,1.2578985203,-0.0950
816884\C,-1.452457485,0.0000308375,-0.0947137127\H,1.7612912862,-1.278
9116364,0.2606547733\H,0.7464588526,-1.2927661556,-1.1905900214\H,0.22
69375104,-2.1647233146,0.2605617832\H,1.7612974538,1.2790542518,0.2603
```

```
034625\H,0.2269480402,2.1648736368,0.2599645205\H,0.7464669535,1.29251
29051,-1.1909462255\H,-1.4927796162,-0.00012188,-1.1905678958\H,-1.988
1646241,0.8859466704,0.2604747346\H,-1.9881712337,-0.8857817464,0.2607
221287\H,0.0001552736,0.0002440563,1.4815832662\\Version=ES64L-G16RevC
.01\HF=-158.373817\RMSD=4.556e-09\RMSF=1.142e-04\Dipole=0.000006,0.000
0072,0.0533798\Quadrupole=-0.1331176,-0.1328825,0.2660002,-0.000001,0.
0001864,0.0000597\PG=C01 [X(C4H10)]\\@
```

2O.M062X

```
1\1\GINC-N1102\FOpt\UM062X\6-31+G(d,p)\C4H9O1(2)\HD_IL182\19-Apr-2021\
0\\#UM062X/6-31+G(d,p) SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) N
osymm\\2o.m062x.freq\\0,2\C,-0.0119582111,0.0207159868,0.0550205583\C,
0.7271759475,-1.2594991718,-0.4010275113\C,0.7339962233,1.2673577824,-
0.4317511075\C,-1.4645588549,-0.0019813231,-0.4317510936\H,1.755365234
6,-1.2587584074,-0.0326030344\H,0.737499032,-1.2773792521,-1.494688671
6\H,0.2124414502,-2.1495677921,-0.0326030246\H,1.7640212055,1.25535608
38,-0.0665013588\H,0.2429822329,2.1694817982,-0.0556432544\H,0.7425736
967,1.3104614431,-1.5252335962\H,-1.5061764936,0.0121421135,-1.5252335
819\H,-2.0003158089,0.8743102748,-0.0556432402\H,-1.9691758884,-0.9000
109146,-0.0665013351\O,0.0361611554,-0.0626290057,1.4371303244\\Versio
n=ES64L-G16RevC.01\HF=-232.9013938\S2=0.753874\S2-1=0.\S2A=0.750012\RM
SD=9.704e-09\RMSF=6.936e-06\Dipole=0.0204586,-0.0354401,-0.8556001\Qua
drupole=0.866449,1.3502422,-2.2166912,-0.4190353,-0.17644,0.3055808\PG
=CS [SG(C2H1O1),X(C2H8)]\\@
```

2OH.a2

```
1\1\GINC-N0706\FOpt\RM062X\6-31+G(d,p)\C4H10O1\HD_IL182\19-Apr-2021\0\
\#M062X/6-31+G(d,p) SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) Nosy
mm\\2oh.m062x.freq\\0,1\C,0.0158008741,0.0113778415,0.2154833001\C,1.5
038563271,0.0060752259,-0.1365370931\C,-0.6665746733,1.2653624859,-0.3
322950511\C,-0.6676793767,-1.2472702991,-0.3045806703\H,1.9995825928,0
.8978180503,0.2649680313\H,1.6511248099,0.0003710103,-1.2210840024\H,1
.9862464487,-0.8781929065,0.2891395499\H,-0.1923115404,2.1696802442,0.
0670249452\H,-1.7217009677,1.2732927039,-0.0450537879\H,-0.5980212637,
1.305088963,-1.4239245793\H,-0.6003647016,-1.3007121351,-1.3950611514\
H,-1.7220115141,-1.2469133598,-0.0146230831\H,-0.1925143779,-2.1343430
713,0.1232163431\O,-0.1428126811,-0.0410740732,1.6349629603\H,0.273425
0439,0.73752932,2.0239172887\\Version=ES64L-G16RevC.01\HF=-233.5755851
\RMSD=6.134e-09\RMSF=2.038e-05\Dipole=0.3014652,0.4586057,-0.3945524\Q
uadrupole=-0.010277,0.7887012,-0.7784242,0.3384742,1.3414199,2.2456144
\PG=C01 [X(C4H10O1)]\\@
```

2OO.a1

```
1\1\GINC-N0721\FOpt\UM062X\6-31+G(d,p)\C4H9O2(2)\HD_IL182\19-Apr-2021\
0\\#UM062X/6-31+G(d,p) SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) N
osymm\\2oo.m062x.freq\\0,2\C,-0.0679388,0.,-0.4516817856\C,0.930394815
1,0.,-1.5982183008\C,-0.9139752974,1.2643279846,-0.4206204322\C,-0.913
9752974,-1.2643279846,-0.4206204322\H,1.5658663168,0.888617102,-1.5558
735526\H,0.3941520243,0.,-2.5509713803\H,1.5658663168,-0.888617102,-1.
5558735526\H,-0.2755946797,2.1517801313,-0.3925740394\H,-1.5626020061,
1.2657044176,0.4579228303\H,-1.5359772132,1.309581431,-1.3189705532\H,
-1.5359772132,-1.309581431,-1.3189705532\H,-1.5626020061,-1.2657044176
,0.4579228303\H,-0.2755946797,-2.1517801313,-0.3925740394\O,0.79949316
9,0.,0.7429164388\O,0.1260245516,0.,1.8548065224\\Version=ES64L-G16Rev
C.01\HF=-308.0420259\S2=0.755118\S2-1=0.\S2A=0.750015\RMSD=3.785e-09\R
MSF=1.391e-05\Dipole=-0.3785131,0.,-1.154907\Quadrupole=0.3526454,1.47
53459,-1.8279913,0.,-0.847758,0.\PG=CS [SG(C2H1O2),X(C2H8)]\\@
```

2OOH.a1b2

```
1\1\GINC-N1525\FOpt\RM062X\6-31+G(d,p)\C4H10O2\HD_IL182\19-Apr-2021\0\
\#M062X/6-31+G(d,p) SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) Nosy
```

mm\\2ooh.m062x.freq\\0,1\C,-0.0963641207,-0.0060344515,-0.4843244958\C
,0.9612244559,-0.005755741,-1.5831747959\C,-0.9318958566,1.2698009008,
-0.5165365003\C,-0.9700791114,-1.2548845168,-0.5584074557\H,1.61344556
91,0.8657918431,-1.483216836\H,0.4747552845,0.0302053358,-2.5618350143
\H,1.5731493393,-0.9104283592,-1.5289127163\H,-0.2821580326,2.14586220
78,-0.4378889525\H,-1.6406485982,1.2843460464,0.3143864815\H,-1.491162
097,1.3291854374,-1.4551605299\H,-1.5005426002,-1.2856218904,-1.514671
5504\H,-1.7127759357,-1.2563446968,0.2432568381\H,-0.3524992025,-2.155
0955646,-0.4772647781\O,0.7075696844,-0.0300751115,0.7104838645\O,-0.1
557306666,0.00348534,1.8471450223\H,0.0351208881,-0.8546237798,2.25112
54187\\Version=ES64L-G16RevC.01\HF=-308.6800467\RMSD=4.303e-09\RMSF=3.
932e-06\Dipole=-0.2703966,-0.5540069,-0.3671236\Quadrupole=-1.4487067,
0.4157486,1.0329581,-0.0937227,-0.2358096,-2.8766713\PG=C01 [X(C4H10O2
)]\\@

TS-2.M062X

1\1\GINC-N0721\FTS\UM062X\6-31+G(d,p)\C7H17(2)\HD_IL182\16-Apr-2021\0\
\#UM062X/6-31+G(d,p) SCF=Tight INT(grid=ultrafine) OPT=(TS,calcfc,noei
gentest,maxcyc=250) IOP(2/17=4) Nosymm\\TS2.m062x.freq\\0,2\C,-0.20707
3949,-0.0342947553,0.5090653565\C,-0.6281792768,-1.4598075901,0.237673
5491\C,-1.1378783107,1.0317413682,-0.0198876347\H,0.0313504116,-2.1785
948796,0.73444654\H,-0.614997913,-1.6863637928,-0.837954415\H,-1.65027
58473,-1.6367367034,0.5927530751\H,-1.225517232,0.9840962396,-1.114804
2512\H,-0.7937971796,2.0368788177,0.2416492135\H,-2.1474373593,0.90257
42582,0.3895388074\C,-0.3755154736,0.2036711064,3.1875922577\C,-0.4734
66044,1.6936158405,3.437899501\C,0.891314695,-0.4231212754,3.729613641
1\C,-1.6351306731,-0.5584800868,3.5400788715\H,0.402652228,2.221108997
9,3.0444364365\H,-0.5310736468,1.9063241751,4.5161907219\H,-1.36736436
07,2.1195786152,2.969506503\H,1.7812641388,0.1017584052,3.365741072\H,
0.9720684335,-1.4755716577,3.4365027448\H,0.9093964881,-0.3834309394,4
.8291951912\H,-1.8383276232,-0.5000111034,4.6203429507\H,-1.5474148279
,-1.6184626722,3.2784547456\H,-2.5081698928,-0.1486927194,3.0195797762
\H,-0.2605204105,0.0937815334,1.8709098127\H,0.8483836255,0.1579888181
,0.2939755332\\Version=ES64L-G16RevC.01\HF=-276.7658388\S2=0.758579\S2
-1=0.\S2A=0.75004\RMSD=5.559e-09\RMSF=7.414e-07\Dipole=0.010937,0.0008
637,-0.0140566\Quadrupole=0.1222508,-0.0233496,-0.0989012,0.0398307,-0
.0861632,-0.0342307\PG=C01 [X(C7H17)]\\@

TS-2O.a2b3

1\1\GINC-N0726\FTS\UM062X\6-31+G(d,p)\C7H17O1(2)\HD_IL182\16-Apr-2021\
0\\#UM062X/6-31+G(d,p) SCF=Tight INT(grid=ultrafine) OPT=(TS,calcfc,no
eigentest,maxcyc=250) IOP(2/17=4) Nosymm\\TS2O.m062x.freq\\0,2\C,-1.13
27448658,-1.093290154,1.8724935734\C,-1.2081865157,0.383687669,2.29220
99556\C,-1.9642489808,-1.9568777933,2.823766084\C,-1.6071145076,-1.253
6107323,0.4259462366\H,-0.8320035311,0.505197432,3.3111221921\H,-2.247
8917521,0.7238806346,2.2537450547\H,-0.605690834,0.9986117645,1.619003
9659\H,-1.5950486732,-1.845322462,3.8470461913\H,-1.890687023,-3.01211
81148,2.5426261976\H,-3.0203452763,-1.6694312552,2.7944782712\H,-2.637
0237884,-0.9010099916,0.3107451185\H,-1.5750522728,-2.3071440064,0.128
2345235\H,-0.9587423537,-0.683527123,-0.2459123755\O,0.2382485179,-1.3
971668067,1.9876014798\C,0.8717696197,-3.6703246577,1.0628463993\C,-0.
1526303158,-4.7730452966,1.2314433899\C,1.2555138196,-3.3602032042,-0.
3691034833\H,-0.4100117088,-4.9336583781,2.2816877743\H,0.2455099766,-
5.7172294838,0.8370345278\H,-1.0725475929,-4.5536673409,0.6783624879\H
,1.7847037202,-4.2117120123,-0.8161434997\H,1.9101767096,-2.4867492493
,-0.4237316857\H,0.3699874346,-3.1630184587,-0.9818849881\H,0.45586697
63,-2.6169947046,1.5410228997\H,1.7499332175,-3.8244462745,1.698929709
2\\Version=ES64L-G16RevC.01\HF=-351.9661435\S2=0.75941\S2-1=0.\S2A=0.7
5004\RMSD=2.249e-09\RMSF=2.483e-06\Dipole=-0.3992758,-0.3645724,-0.265
827\Quadrupole=-0.3320625,3.3711144,-3.0390519,-0.5419263,-1.9664272,0
.1997586\PG=C01 [X(C7H17O1)]\\@

```
TS-2OO.a1b3
 1\1\GINC-N1608\FTS\UM062X\6-31+G(d,p)\C7H17O2(2)\HD_IL182\16-Apr-2021\
 0\\#UM062X/6-31+G(d,p) SCF=Tight INT(grid=ultrafine) OPT=(TS,calcfc,no
 eigentest,maxcyc=250) IOP(2/17=4) Nosymm\\TS2OO.m062x.freq\\0,2\C,-0.1
 40858476,-0.696987602,0.0395060845\C,0.4726425513,-1.9072665063,-0.655
 6350167\C,-0.7991742533,0.2439632833,-0.9619735453\C,-1.1115639999,-1.
 1159894886,1.1389075361\H,1.182843282,-1.5866570993,-1.4246823749\H,-0
 .3124726772,-2.4977432586,-1.1371527812\H,0.9906336199,-2.544817423,0.
 0656262605\H,-0.0780125802,0.5605813145,-1.7211780429\H,-1.1836696159,
 1.132107118,-0.4534310568\H,-1.6310842189,-0.2638056985,-1.4579476212\
 H,-1.9378465562,-1.693730004,0.7137377454\H,-1.5196255116,-0.231595870
 7,1.6361733497\H,-0.5986124587,-1.7300705674,1.8827232713\O,0.89769856
 1,0.1302834639,0.6132983159\O,1.6196911633,-0.5807760516,1.5583306084\
 C,3.8325006224,-0.9374171382,0.4072224439\C,3.7711683036,0.1312485266,
 -0.6534849149\C,4.0296097362,-2.3561607742,-0.0647378678\H,3.022972633
 7,-0.1110095092,-1.4155090559\H,4.7423738072,0.2226528118,-1.160787916
 5\H,3.5151997181,1.1047585818,-0.2282037868\H,3.3270492824,-2.61180771
 97,-0.8636091387\H,3.9082390319,-3.0772069411,0.7483556055\H,5.0439341
 595,-2.4818746189,-0.4696045047\H,2.6445727558,-0.8403459724,1.0121275
 119\H,4.4618211195,-0.6699428562,1.2616288911\\Version=ES64L-G16RevC.0
 1\HF=-427.0850288\S2=0.759754\S2-1=0.\S2A=0.750048\RMSD=6.729e-09\RMSF
 =4.041e-06\Dipole=0.1153613,-0.4768453,-0.6967255\Quadrupole=4.4107031
 ,-0.7494791,-3.661224,-1.5263038,-1.1910483,0.0022387\PG=C01 [X(C7H17O
 2)]\\@
```

Cis-pent-2-ene

```
5.M062X
 1\1\GINC-R37\FOpt\UM062X\6-31+G(d,p)\C5H9(2)\ROOT\09-May-2018\0\\# M06
 2X/6-31+G** SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=6710
 88640\\5.M062X\\0,2\C,1.4943591788,5.9875319483,-0.8287535531\C,1.1465
 271703,4.7743825845,-1.6339915567\C,0.9923244583,3.5060361984,-1.07980
 69219\C,1.1347474666,3.1955140869,0.2587514456\C,0.9608170827,1.819961
 7233,0.8173283917\H,1.5714286355,6.8761754487,-1.4576077415\H,2.451965
 4726,5.8608286826,-0.3070565258\H,0.7388177149,6.1863784828,-0.0573890
 046\H,1.0068644361,4.8895907148,-2.7038094564\H,0.7380854954,2.6914762
 79,-1.7579728059\H,1.3880834765,3.9872768137,0.9610440283\H,0.16482385
 17,1.7915989351,1.571372288\H,1.874460355,1.4707389657,1.3135985345\H,
 0.7078252057,1.1034491362,0.0310128778\\Version=ES64L-G09RevE.01\State
 =2-A\HF=-195.7977532\S2=0.77929\S2-1=0.\S2A=0.750195\RMSD=3.395e-09\RM
 SF=3.223e-05\Dipole=0.0199084,0.0175719,0.1143708\Quadrupole=-2.028581
 5,1.1464364,0.8821451,0.5579966,0.3801833,-0.4368906\PG=C01 [X(C5H9)]\
 \@

5h.M062X
 1\1\GINC-R42\FOpt\RM062X\6-31+G(d,p)\C5H10\ROOT\09-May-2018\0\\# M062X
 /6-31+G** SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=671088
 640\\5h.M062X\\0,1\C,1.5554316892,5.8535490298,-0.7279229827\C,1.09659
 28502,4.5502583657,-1.3281775236\C,1.165249104,3.3801611927,-0.6879006
 891\C,1.7072508502,3.2117497994,0.7098414025\C,1.6649938493,1.76222564
 04,1.1906610375\H,1.4117423844,6.6877872982,-1.4168675072\H,2.61882408
 47,5.815985924,-0.4634666444\H,1.0066185261,6.0809474988,0.1936222288\
 H,0.6894947098,4.5734240688,-2.3363575932\H,0.8119982465,2.4807943599,
 -1.1919654468\H,1.138155246,3.8479851671,1.4016758832\H,2.7400519786,3
 .5847178196,0.7487885925\H,0.6378998321,1.3839555393,1.1926810729\H,2.
 0621849858,1.6651319001,2.2043441109\H,2.25675804,1.1179006197,0.53288
 07701\\Version=ES64L-G09RevE.01\State=1-A'\HF=-196.4374243\RMSD=3.693e
 -09\RMSF=1.617e-05\Dipole=0.0593501,0.0769389,0.1145943\Quadrupole=-0.
 9183326,0.6610571,0.2572755,0.1699432,0.525658,-0.3175531\PG=CS [SG(C5
 H4),X(H6)]\\@
```

5o.M062X
1\1\GINC-R38\FOpt\UM062X\6-31+G(d,p)\C5H9O1(2)\ROOT\09-May-2018\0\\# M
062X/6-31+G** SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=67
1088640\\5o.M062X\\0,2\C,1.5670612588,5.9898387241,-0.8879831078\C,1.1
675903853,4.7287865126,-1.5914492649\C,1.0966148369,3.5093658716,-1.05
04320117\C,1.4079114779,3.2068963189,0.4127578206\C,0.8638063742,1.846
8917111,0.8363720957\H,0.7624594474,6.7312108267,-0.935227997\H,2.4385
696547,6.4302928261,-1.3830428055\H,1.834798113,5.8136203959,0.1549579
227\H,0.9161446262,4.8261509763,-2.6469913539\H,0.8551603421,2.6469467
427,-1.6671824821\H,0.9891196394,4.0046005594,1.0465716608\O,2.7908804
236,3.2444579245,0.4260950479\H,-0.2285591413,1.8421731913,0.772490540
6\H,1.1533721082,1.6246576171,1.8660816546\H,1.2656204536,1.0656398016
,0.1852122798\\Version=ES64L-G09RevE.01\State=2-A\HF=-270.9623839\S2=0
.754981\S2-1=0.\S2A=0.750018\RMSD=6.655e-09\RMSF=1.371e-05\Dipole=-0.7
915026,0.234292,-0.2118708\Quadrupole=-3.6157347,2.0196012,1.5961335,1
.2046422,-0.7337504,-0.9231922\PG=C01 [X(C5H9O1)]\\@

5oh.M062X
1\1\GINC-R37\FOpt\RM062X\6-31+G(d,p)\C5H10O1\ROOT\09-May-2018\0\\# M06
2X/6-31+G** SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=6710
88640\\5oh.M062X\\0,1\C,1.657453985,5.9611847996,-0.9313917678\C,1.094
0957901,4.7394327567,-1.5957857505\C,0.9294627475,3.5442736114,-1.0207
367149\C,1.3158000761,3.21925046,0.4080766747\C,0.9095840441,1.8009098
106,0.7886139269\H,0.9496691029,6.7940029185,-1.0015059097\H,2.5758651
583,6.2805666988,-1.4361686301\H,1.9017324709,5.7805122405,0.116373310
9\H,0.7956650586,4.8521652197,-2.6375236682\H,0.5003076888,2.732371467
3,-1.6072060248\H,0.8239594948,3.9243731823,1.0892052738\O,2.708798584
,3.4259847375,0.6420808604\H,-0.1733042822,1.6693877558,0.6981260741\H
,1.2087295972,1.5868271318,1.816741641\H,1.3971751334,1.0751757224,0.1
273269424\H,3.1995853505,3.0245614871,-0.0852062384\\Version=ES64L-G09
RevE.01\State=1-A\HF=-271.6352642\RMSD=6.370e-09\RMSF=1.510e-05\Dipole
=-0.2493376,-0.1329456,-0.5236556\Quadrupole=-0.8305105,1.5408962,-0.7
103857,-0.3627775,-2.1318613,-0.3534716\PG=C01 [X(C5H10O1)]\\@

5oo.a3
1\1\GINC-R39\FOpt\UM062X\6-31+G(d,p)\C5H9O2(2)\ROOT\08-May-2018\0\\#M0
62X/6-31+G** SCF=Tight IOP(2/17=4) INT(grid=ultrafine) OPT maxdisk=671
088640\\a3\\0,2\C,1.3018049857,6.0885218056,-0.8799598342\C,1.13746229
22,4.7780734225,-1.5885675217\C,1.203161796,3.5499597561,-1.0664919986
\C,1.447759392,3.226831095,0.3764653357\C,0.7575498884,1.9557801162,0.
8316063931\H,0.4337153698,6.7318915801,-1.0565708794\H,2.1781142273,6.
6113907926,-1.2772474239\H,1.451606208,5.9765202677,0.1939735516\H,0.9
592302468,4.8492663604,-2.661150183\H,1.0924765553,2.6899640787,-1.725
2024496\H,1.201183195,4.068459369,1.0282644565\O,2.8811799079,2.977896
4433,0.593213098\H,-0.3241443646,2.0726666055,0.7312179997\H,0.9948117
286,1.7358256559,1.874701919\H,1.0732890989,1.1106493608,0.2132458471\
O,3.5806124727,4.0668652904,0.4731196895\\Version=ES64L-G09RevE.01\Sta
te=2-A\HF=-346.1010742\S2=0.755157\S2-1=0.\S2A=0.750016\RMSD=4.177e-09
\RMSF=2.430e-06\Dipole=-1.1232979,0.0202637,-0.1857241\Quadrupole=-4.1
468705,2.3855442,1.7613263,0.629845,-1.4291947,-0.8828909\PG=C01 [X(C5
H9O2)]\\@

5ooh.a3
1\1\GINC-R47\FOpt\RM062X\6-31+G(d,p)\C5H10O2\ROOT\08-May-2018\0\\#M062
X/6-31+G** SCF=Tight IOP(2/17=4) INT(grid=ultrafine) OPT maxdisk=67108
8640\\a3\\0,1\C,1.0588497961,6.0942683656,-0.8731782909\C,1.0744543174
,4.7561029666,-1.5538862484\C,1.29026855,3.561167459,-0.9934052819\C,1
.5792980254,3.2940211812,0.459875682\C,0.9219254594,2.0142741089,0.950
5211881\H,1.7445746436,6.7804525372,-1.3811446442\H,1.3600126646,6.038
1112057,0.1731305271\H,0.061241426,6.5429364398,-0.9322477991\H,0.8843

065771,4.7767440276,-2.6269626987\H,1.2859138542,2.677113745,-1.631551
4976\H,1.2817134881,4.1398674407,1.0888057773\O,2.9839533594,3.0794367
133,0.6564540219\H,-0.1634431963,2.0967873978,0.8531554022\H,1.1742703
768,1.8330508632,1.997410736\H,1.2608985135,1.1614754536,0.3550386596\
O,3.6461019036,4.316758541,0.4358090947\H,3.8410202412,4.2789635538,-0
.5139386281\\Version=ES64L-G09RevE.01\State=1-A\HF=-346.7420759\RMSD=7
.992e-09\RMSF=6.696e-06\Dipole=-0.6793023,0.2069437,-0.7128972\Quadrup
ole=-1.9042534,1.1993768,0.7048766,0.7342867,-3.4549006,-1.0003513\PG=
C01 [X(C5H10O2)]\\@

TS-5-u.a2

1\1\GINC-R52\FTS\UM062X\6-31+G(d,p)\C10H19(2)\ROOT\10-May-2018\0\\#M06
2X/6-31+G** SCF=Tight IOP(2/17=4) INT(grid=ultrafine) OPT(TS,calcfc,ma
xstep=15,noeigentest,maxcyc=200) maxdisk=1073741824\\a2\\0,2\C,3.65217
12966,1.1237192929,0.9477959673\C,3.0773929801,1.9698430149,2.04512780
35\C,2.526194951,3.1923904606,1.8986172686\C,2.4075824219,3.9535109533
,0.6576543914\C,1.4975927392,5.1609494392,0.6507900616\H,3.1482417724,
0.152025031,0.8949124218\H,4.7132527626,0.9195197363,1.132548182\H,3.5
713053073,1.6012355799,-0.0311620213\H,3.1196534288,1.5473687205,3.047
075708\H,2.1797906062,3.6988763088,2.8006190496\H,2.3497040931,3.35693
93873,-0.2563209853\H,0.4409942651,4.8724390334,0.5970898507\H,1.71151
45015,5.8041186546,-0.209641606\H,1.6340618958,5.7552127896,1.56077146
93\H,3.6151099001,4.5044683401,0.4462126041\C,5.182364363,3.764358498,
-2.4990472403\C,4.8652760778,5.2074012123,-2.2392008688\C,4.7169475273
,5.7815473623,-1.0274805155\C,4.7991601817,5.1157128495,0.2699141665\C
,4.9015359846,5.9809819679,1.5055699237\H,6.1043738837,3.6627564274,-3
.0825790648\H,4.3845611159,3.2926022003,-3.0844348105\H,5.3003197223,3
.1919132973,-1.5763776212\H,4.742191481,5.8361244966,-3.1188180174\H,4
.4534655788,6.8398682811,-1.0016476136\H,5.435848984,4.2279730106,0.30
35411988\H,5.9105072948,6.3918885975,1.6307246087\H,4.6628717447,5.403
7074467,2.4053186968\H,4.2041621388,6.8237366102,1.4483319923\\Version
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5884\Quadrupole=-1.982113,0.9178131,1.0642999,-1.8002656,0.383032,0.73
77372\PG=C01 [X(C10H19)]\\@

TS-5o-u.a2b2

1\1\GINC-R45\FTS\UM062X\6-31+G(d,p)\C10H19O1(2)\ROOT\09-May-2018\0\\#M
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noeigentest,maxcyc=200) maxdisk=1073741824\\a2 b2\\0,2\C,0.2066579811,
5.7557628313,0.121825624\C,1.0530913838,5.0470082238,-0.8915487805\C,1
.9790454258,4.1212090167,-0.6310256486\C,2.3280651927,3.6113462996,0.7
587074331\C,3.0932930035,2.2947243764,0.6830885775\H,-0.8585980384,5.6
060906136,-0.0846909866\H,0.3950642978,6.8337288629,0.0789721654\H,0.4
255235695,5.4233035338,1.137738843\H,0.8980993964,5.3316202236,-1.9316
877878\H,2.5747569877,3.7122534827,-1.445054676\H,1.4002206218,3.46726
46157,1.3389785088\O,3.0932506754,4.6421991516,1.324393224\H,2.4996051
06,1.5341124675,0.1662463148\H,3.3248092612,1.9251905855,1.6857293216\
H,4.0313964224,2.4449279694,0.1395895981\H,3.3921996037,4.2386187705,2
.6139761939\C,0.5622111767,4.4847756598,3.9082277191\C,1.2019529378,3.
153859905,4.176021889\C,2.519059583,2.9071330963,4.103754786\C,3.55833
21393,3.9102623283,3.7551767915\C,4.9923042262,3.4265285567,3.87743800
97\H,0.2464793371,4.9637050413,4.8429859946\H,-0.3375742751,4.36298688
99,3.2959642116\H,1.2412898005,5.1642542586,3.3854591209\H,0.537070171
,2.3363728315,4.4488327446\H,2.8652656501,1.8891704817,4.2868469968\H,
3.4006501323,4.867480987,4.2642666645\H,5.2370220133,3.1965714862,4.92
10829627\H,5.6948258833,4.1835321907,3.521819666\H,5.1493383341,2.5167
772626,3.289024518\\Version=ES64L-G09RevE.01\State=2-A\HF=-467.3971839
\S2=0.761834\S2-1=0.\S2A=0.750089\RMSD=8.647e-09\RMSF=1.004e-06\Dipole
=-0.4556531,-0.3131089,0.2379299\Quadrupole=0.2765244,-1.0631544,0.786
63,-2.4615282,1.2266629,0.0098495\PG=C01 [X(C10H19O1)]\\@

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TS-5oo-u.a2b3
 1\1\GINC-R74\FTS\UM062X\6-31+G(d,p)\C10H19O2(2)\ROOT\09-May-2018\0\\#M
 062X/6-31+G** SCF=Tight IOP(2/17=4) INT(grid=ultrafine) OPT(TS,calcfc,
 noeigentest,maxcyc=200) maxdisk=1610612736\\a2 b3 c1\\0,2\C,-0.6023456
 57,5.4256654527,-0.1439103694\C,0.7406443419,5.2564832251,-0.792899443
 7\C,1.7450373231,4.4722117303,-0.39341432\C,1.7503734707,3.5511975109,
 0.7909857687\C,1.825897366,2.0856669827,0.3826111056\H,-1.3958972295,5
 .0503786718,-0.7993510568\H,-0.8106184285,6.4871340608,0.0287671589\H,
 -0.6779719901,4.9048979069,0.8123301322\H,0.8960014381,5.8410120589,-1
 .6989200899\H,2.6642779266,4.4543171704,-0.9785523019\H,0.8865800068,3
 .7223224559,1.4431652529\O,2.9256798153,3.9201253276,1.5384986251\H,0.
 91550832,1.8006384222,-0.1517493924\H,1.9349868071,1.4574458382,1.2692
 416811\H,2.6844869154,1.9227500875,-0.2756537724\O,2.9439071636,3.2408
 467962,2.7300069744\H,2.3985870492,4.0647247119,3.5188816627\C,3.23175
 20882,6.9336741447,2.1805506095\C,1.7665183565,6.6781422011,2.34394255
 71\C,1.1935186522,5.8475256366,3.2395465524\C,1.8956802253,5.018702743
 4,4.2208514021\C,1.0505088405,4.3616280285,5.292545454\H,3.5301050569,
 6.7059446088,1.1515963454\H,3.83904144,6.3118039844,2.8400190339\H,3.4
 659399679,7.9882993931,2.3658294907\H,1.1098070737,7.2111042736,1.6576
 464428\H,0.1090002825,5.729348127,3.199620488\H,2.8221278677,5.4576256
 086,4.6004990112\H,0.6544159373,5.1086255034,5.9912926816\H,1.63191198
 4,3.6386275277,5.8697513005\H,0.1992105886,3.8355168089,4.8489490156\\
 Version=ES64L-G09RevE.01\State=2-A\HF=-542.520514\S2=0.766769\S2-1=0.\
 S2A=0.750175\RMSD=8.505e-09\RMSF=2.575e-06\Dipole=-0.8574518,0.5009934
 ,-0.2643914\Quadrupole=-1.3988261,-1.326024,2.7248501,2.0307703,0.2498
 722,-0.4424081\PG=C01 [X(C10H19O2)]\\@
```


S2. Details of kinetic Monte Carlo (*k*MC) modelling framework

S2.1. Representation of population of macromolecules using bivariate binary tree structures

As mentioned in the main text, each population considered in the kinetic Monte Carlo (*k*MC) model is tracked by two distribution variables, being (i) the carbon number of the polymer backbone (CN) and (ii) the number of defects (*e.g.* allylic, tertiary or quaternary carbon atoms; in main text only example with allylic (poly(butadiene)) and quaternary (poly(isobutylene)) carbon atoms). To store all this information for every population type, bivariate binary trees are used. An example is given below, considering the population P_i with 6 species (CN = 4; note that the primary C atoms at chain ends are not considered in CN calculation and thus also not shown) as defined in Figure S1a (pol(ethylene) with tertiary defects; green: secondary hydrogen (H) atoms; orange: tertiary H atoms). The representation of the population P_i in a bivariate tree is shown in Figure S1b on the left. A schematic representation of the relation with the distribution of the population is shown in Figure S1b on the right.

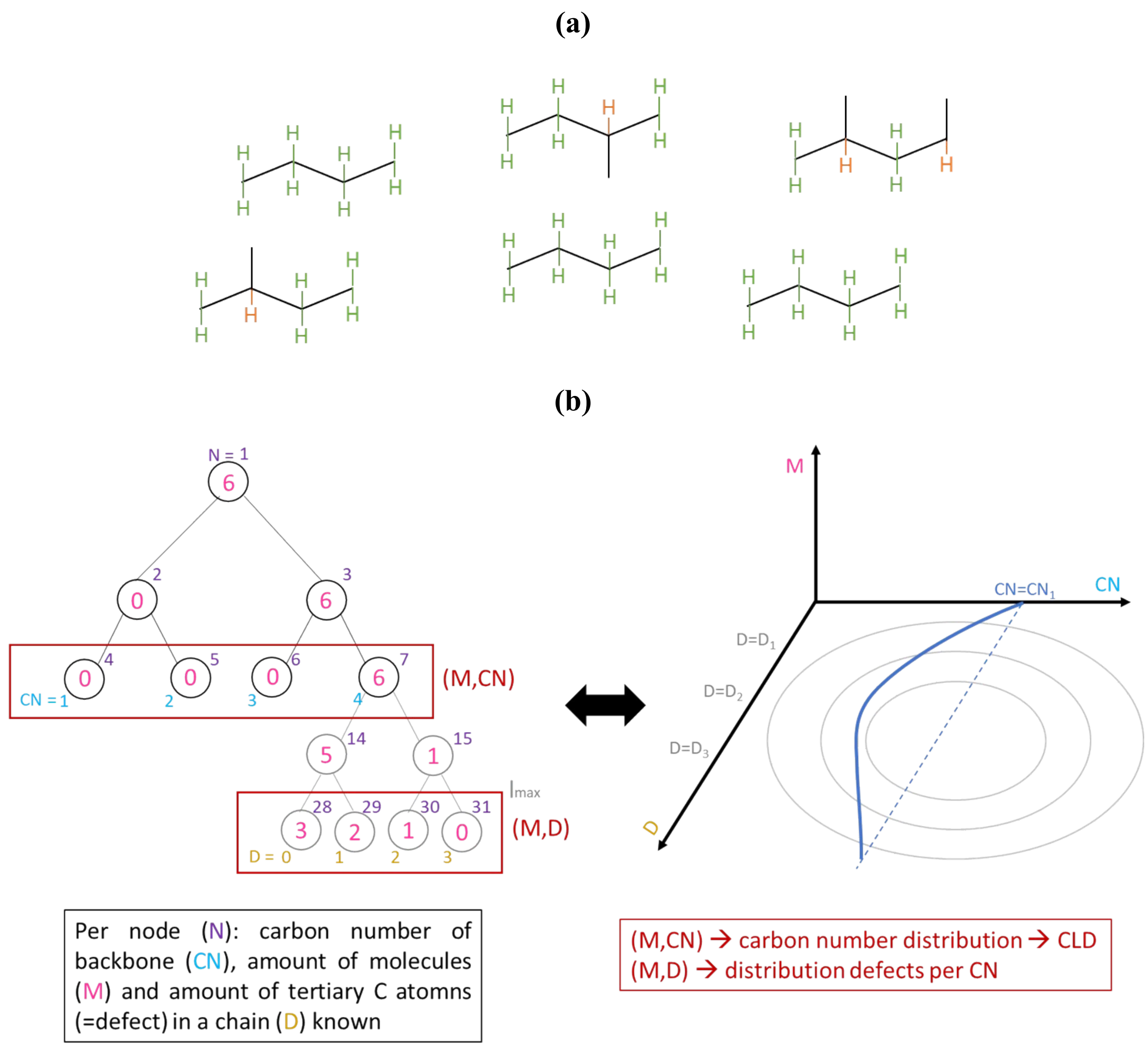


Figure S1. **(a)** Population P_i (poly(ethylene) with tertiary defects) consisting of 6 species with CN = 4; secondary H atoms are shown in green and tertiary in orange and **(b)** representation of population P_i in bivariate binary tree (left) and relation with the distribution of population P_i (right).

S2.2. Example of the use of mass-weighted binary trees

As the hydrogen abstraction reaction involves macromolecules with multiple reactive centres, mass-weighted binary trees are used additionally to the number-weighted tree as shown in Figure S2b on the left, to properly calculate its total reaction probability and to properly select the specific reaction partners to undergo the reaction. This is necessary because larger macromolecules have a larger probability to undergo hydrogen abstraction compared to smaller molecules, as was also explained in the main text. In Figure S2, related to the example defined in Figure S1, it is shown how mass-weighted trees (right part of Figure S2) are constructed starting from the corresponding number-weighted tree (left part of Figure S2; taken from Figure

S1) and how their information is used to calculate the reaction rate for hydrogen abstraction of tertiary H atoms ($r_{abstertH}$ (mol L^{-1} s^{-1}); top of right part of Figure S2; with k_{absH} (L mol^{-1} s^{-1}) the single-event rate coefficient for H abstraction reaction, $n_{H,tertC}$ the number of H atoms per tertiary C atom, n_{tertC} the total number of tertiary C atom, V the volume (L) and N_{Av} the constant of Avogadro (mol^{-1})) and for hydrogen abstraction of secondary H atoms ($r_{abssecH}$ (mol L^{-1} s^{-1}); bottom of right part of Figure S2; with k_{absH} (L mol^{-1} s^{-1}) the single-event rate coefficient for H abstraction reaction, $n_{H,secC}$ the number of H atoms per secondary C atom, n_{secC} the total number of secondary C atom, V the volume (L) and N_{Av} the constant of Avogadro (mol^{-1})).

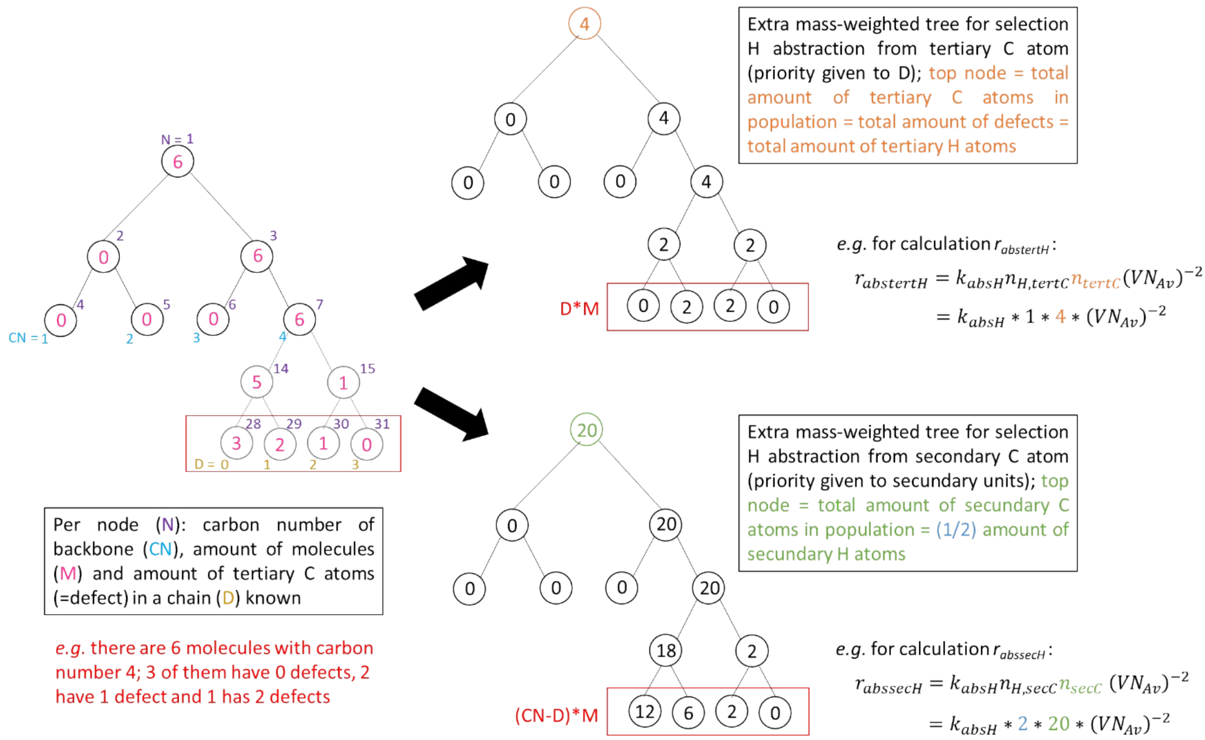


Figure S2. Construction of mass-weighted bivariate trees (right) based on the corresponding number-weighted bivariate tree (left; taken from Figure S1) and calculation of reaction rate for hydrogen abstraction of tertiary H atoms ($r_{abstertH}$ (mol L^{-1} s^{-1}) with k_{absH} (L mol^{-1} s^{-1}) the single-event rate coefficient for H abstraction reaction, $n_{H,tertC}$ the number of H atoms per tertiary carbon (C) atom, n_{tertC} the total number of tertiary C atom, V the volume (L) and N_{Av} the constant of Avogadro (mol^{-1}), and for hydrogen abstraction of secondary H atoms ($r_{abssecH}$ (mol L^{-1} s^{-1}) with k_{absH} (L mol^{-1} s^{-1}) the single-event rate coefficient for H abstraction reaction, $n_{H,secC}$ the number of H atoms per secondary C atom, n_{secC} the total number of secondary C atom, V the volume (L) and N_{Av} the Avogadro number (mol^{-1}).

S3. Model parameters for autoxidation simulations

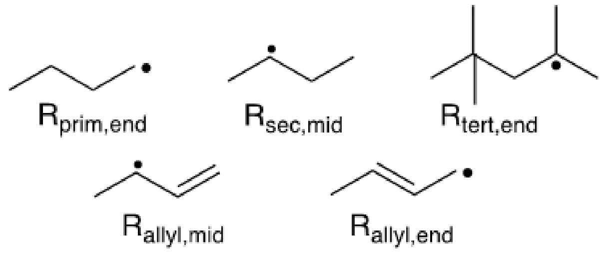


Figure S3. Representation of radical types considered in *k*MC model, a differentiation is made according to their endgroup; see Table S4 to S6 for reaction schemes.

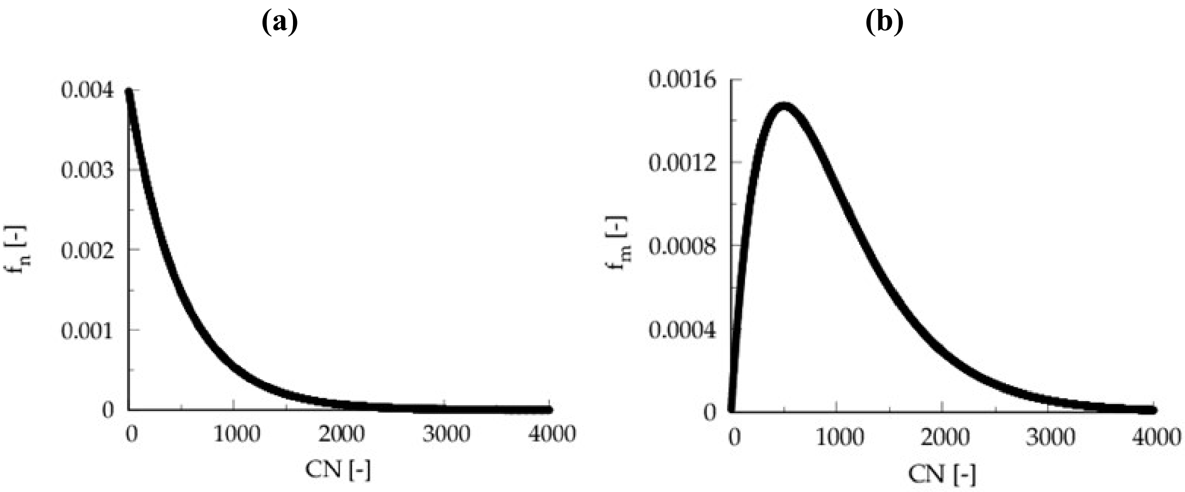


Figure S4. Chain length distribution (CLD) of initial polymer: **(a)** on number fraction basis $f_{n,CN}$ and **(b)** on mass fraction basis $f_{m,CN}$; expressed in carbon number (CN) instead of chain length *i* (see Figure 1 in main text; example shown for poly(ethylene) and poly(isobutylene) for which CN = 2**i* .

Table S4. Reaction mechanism for the autoxidation of poly(butadiene); also given are the rate coefficients ((L mol^{-1}) s^{-1}) at 298 K; P = dead polymer chain, R* = polymer alkyl radical; RO* = polymer alkoxy radical; RO_2^* = polymer alkyl peroxyl radical; endgroups according to Figure S3; *i* and *j* represent carbon number; no reactions with $C_{/\!/}$ accounted for in model.

Reaction	***Reaction Equation***	k_f **((L mol^{-1}) s^{-1})**	k_r **((L mol^{-1}) s^{-1})**	***Ref***
Initiation	$P_i \rightleftharpoons R_{allyl,end,j} + R_{allyl,end,i-j}$	1.0 10^{-10}	1.2 10^{2}	a, b
Propagation	$R_{allyl,end,i} + O_2 \rightleftharpoons R_{allyl,end,i}O_2^*$	4.0 10^{6}	0.0	1
	$R_{allyl,mid,i} + O_2 \rightleftharpoons R_{allyl,mid,i}O_2^*$	4.0 10^{6}	0.0	1
	$R_{allyl,end,i}O_2^* + R_{allyl,end,j}O_2^* \rightleftharpoons R_{allyl,end,i}O^* + R_{all}$	0.0	0.0	2
	$R_{allyl,end,i}O_2^* + R_{allyl,mid,j}O_2^* \rightleftharpoons R_{allyl,end,i}O^* + R_{all}$	0.0	0.0	2
	$R_{allyl,mid,i}O_2^* + R_{allyl,mid,j}O_2^* \rightleftharpoons R_{allyl,mid,i}O^* + R_{all}$	0.0	0.0	2
H-	$R_{allyl,end,i}O_2^* + P_{allylH,j} \rightleftharpoons R_{allyl,end,i}OOH + R_{allyl,mid}$	9.0 10^{-2}	1.1 10^{-4}	c

abstraction	$R_{allyl,mid,i}O_2{}^{*} + P_{allylH,j} \rightleftharpoons R_{allyl,mid,i}OOH + R_{allyl,mi}$	9.0 10^{-2}	1.1 10^{-4}	c
	$R_{allyl,end,i} + P_{allylH,j} \rightleftharpoons P_i + R_{allyl,mid,j}$	9.6 10^{-6}	9.6 10^{-6}	c
	$R_{allyl,mid,i} + P_{allylH,j} \rightleftharpoons P_i + R_{allyl,mid,j}$	9.6 10^{-6}	9.6 10^{-6}	c
	$R_{allyl,end,i}O^{*} + P_{allylH,j} \rightleftharpoons R_{allyl,end,i}OH + R_{allylid,j}$	3.4 10^{5}	3.5 10^{-12}	c
	$R_{allyl,mid,i}O^{*} + P_{allylH,j} \rightleftharpoons R_{allyl,mid,i}OH + R_{allyl,mid,j}$	3.4 10^{5}	3.5 10^{-12}	c
β-scission	$R_{allyl,mid,i} \rightleftharpoons P_j + R_{allyl,end,i-j}$	6.8 10^{-14}	0.0	3
Termination[d]	$R_{allyl,end,i}O_2{}^{*} + R_{allyl,end,j} \rightleftharpoons R_{allyl,end,i}OOR_{allyl,end,j}$	1.2 10^{2}	0.0	b
	$R_{allyl,end,i}O_2{}^{*} + R_{allyl,mid,j} \rightleftharpoons R_{allyl,end,i}OOR_{allyl,mid,j}$	1.2 10^{2}	0.0	b
	$R_{allyl,mid,i}O_2{}^{*} + R_{allyl,end,j} \rightleftharpoons R_{allyl,mid,i}OOR_{allyl,end,j}$	1.2 10^{2}	0.0	b
	$R_{allyl,mid,i}O_2{}^{*} + R_{allyl,mid,j} \rightleftharpoons R_{allyl,mid,i}OOR_{allyl,mid,j}$	1.2 10^{2}	0.0	b
	$R_{allyl,end,i}O_2{}^{*} + R_{allyl,end,j}O_2{}^{*} \rightleftharpoons R_{allyl,end,i}C(O)H +$	6.4 10^{6}	0.0	4
	$R_{allyl,end,i}O_2{}^{*} + R_{allyl,mid,j}O_2{}^{*} \rightleftharpoons R_{allyl,end,i}C(O)H +$	6.4 10^{6}	0.0	4
	$R_{allylmid,i}O_2{}^{*} + R_{allyl,end,j}O_2{}^{*} \rightleftharpoons R_{allyl,mid,k}C(O)R_{ally}$	6.4 10^{6}	0.0	4
	$R_{allyl,mid,i}O_2{}^{*} + R_{allyl,mid,j}O_2{}^{*} \rightleftharpoons R_{allyl,mid,k}C(O)R_{all}$	6.4 10^{6}	0.0	4
Re-initiation	$R_{allyl,end,i}OOR_{allyl,end,j} \rightleftharpoons R_{allyl,end,i}O^{*} + R_{allyl,end,j}O^{*}$	2.6 10^{-11}	0.0	5
	$R_{allyl,end,i}OOR_{allyl,mid,j} \rightleftharpoons R_{allyl,end,i}O^{*} + R_{allyl,mid,j}O$	2.6 10^{-11}	0.0	5
	$R_{allyl,mid,i}OOR_{allyl,mid,j} \rightleftharpoons R_{allyl,mid,i}O^{*} + R_{allyl,mid,j}O$	2.6 10^{-11}	0.0	5

[a]Forward rate coefficient: value chosen to reach realistic timescales (approximately one month is required to reduce the average chain length by a factor two); [b]Reverse rate coefficient: calculated using diffusion coefficient from Roland *et al.*[6] and Smoluchowski relationship (r = 4.7 10^{-10} m); [c]Calculated in this work; see Table S1.

Table S5. Reaction mechanism for the autoxidation of poly(ethylene); also given are the rate coefficients ((L mol^{-1}) s^{-1}) at 298 K; P = dead polymer chain, R* = polymer alkyl radical; RO* = polymer alkoxy radical; RO$_2^*$ = polymer alkyl peroxyl radical; endgroups according to Figure S3; *i* and *j* represent carbon number.

Reaction	***Reaction Equation***	k_f **((L mol^{-1}) s^{-1})**	k_r **((L mol^{-1}) s^{-1})**	***Ref***
Initiation	$P_i \rightleftharpoons R_{prim,end,j} + R_{prim,end,i-j}$	1.0 10^{-10}	1.2 10^{2}	a, b
Propagation	$R_{prim,end,i} + O_2 \rightleftharpoons R_{prim,end,i}O_2{}^*$	4.0 10^{6}	0.0	1
	$R_{sec,mid,i} + O_2 \rightleftharpoons R_{sec,mid,i}O_2{}^*$	4.0 10^{6}	0.0	1
	$R_{prim,end,i}O_2{}^* + R_{prim,end,j}O_2{}^* \rightleftharpoons R_{prim,end,i}O^* + R_{p}$	0.0	0.0	7
	$R_{prim,end,i}O_2{}^* + R_{sec,mid,j}O_2{}^* \rightleftharpoons R_{prim,end,i}O^* + R_{sec}$	0.0	0.0	7
	$R_{sec,mid,i}O_2{}^* + R_{sec,mid,j}O_2{}^* \rightleftharpoons R_{sec,mid,i}O^* + R_{sec,mi}$	0.0	0.0	7
H-abstraction	$R_{prim,end,i}O_2{}^* + P_{secH,j} \rightleftharpoons R_{prim,end,i}OOH + R_{sec,mid,j}$	1.8 10^{-9}	3.6 10^{0}	d
	$R_{sec,mid,i}O_2{}^* + P_{secH,j} \rightleftharpoons R_{sec,mid,i}OOH + R_{sec,mid,j}$	2.7 10^{-8}	1.6 10^{1}	c
	$R_{prim,end,i} + P_{secH,j} \rightleftharpoons P_i + R_{sec,mid,j}$	7.9 10^{-7}	3.7 10^{-7}	d
	$R_{sec,mid,i} + P_{secH,j} \rightleftharpoons P_i + R_{sec,mid,j}$	1.2 10^{-4}	1.2 10^{-4}	c
	$R_{prim,end,i}O^* + P_{secH,j} \rightleftharpoons R_{prim,end,i}OH + R_{sec,mid,j}$	3.7 10^{2}	4.7 10^{-4}	d
	$R_{sec,mid,i}O^* + P_{secH,j} \rightleftharpoons R_{sec,mid,i}OH + R_{sec,mid,j}$	3.8 10^{2}	9.2 10^{-5}	c
β-scission	$R_{sec,mid,i} \rightleftharpoons P_j + R_{prim,end,i-j}$	8.7 10^{-8}	0.0	3
Termination	$R_{prim,end,i}O_2{}^* + R_{prim,end,j} \rightleftharpoons R_{prim,end,i}OOR_{prim,end,j}$	1.2 10^{2}	0.0	b
	$R_{prim,end,i}O_2{}^* + R_{sec,mid,j} \rightleftharpoons R_{prim,end,i}OOR_{sec,mid,j}$	1.2 10^{2}	0.0	b
	$R_{sec,mid,i}O_2{}^* + R_{prim,end,j} \rightleftharpoons R_{sec,mid,i}OOR_{prim,end,j}$	1.2 10^{2}	0.0	b
	$R_{sec,mid,i}O_2{}^* + R_{sec,mid,j} \rightleftharpoons R_{sec,mid,i}OOR_{sec,mid,j}$	1.2 10^{2}	0.0	b
	$R_{prim,end,i}O_2{}^* + R_{prim,end,j}O_2{}^* \rightleftharpoons R_{prim,end,i}C(O)H +$	1.6 10^{6}	0.0	8
	$R_{prim,end,i}O_2{}^* + R_{sec,mid,j}O_2{}^* \rightleftharpoons R_{prim,end,i}C(O)H +$	1.6 10^{6}	0.0	8
	$R_{sec,mid,i}O_2{}^* + R_{prim,end,j}O_2{}^* \rightleftharpoons R_{sec,mid,k}C(O)R_{sec,m}$	1.6 10^{6}	0.0	8
	$R_{sec,mid,i}O_2{}^* + R_{sec,mid,j}O_2{}^* \rightleftharpoons R_{sec,mid,k}C(O)R_{sec,mi}$	1.6 10^{6}	0.0	8
Re-initiation	$R_{prim,end,i}OOR_{prim,end,j} \rightleftharpoons R_{prim,end,i}O^* + R_{prim,end,j}O$	8.4 10^{-13}	0.0	5
	$R_{prim,end,i}OOR_{sec,mid,j} \rightleftharpoons R_{prim,end,i}O^* + R_{sec,mid,j}O^*$	8.4 10^{-13}	0.0	5

[a]Forward rate coefficient: value chosen to reach realistic timescales (approximately one month is required to reduce the average chain length by a factor two); [b]Reverse rate coefficient: calculated using diffusion coefficient from Roland *et al.*[6] and Smoluchowski relationship (r = 4.7 10^{-10} m); [c]Calculated in this work; see Table S1; [d]H abstraction rate coefficients for primary radicals are calculated based on results for secondary and tertiary radicals (Table S1) assuming a geometric average for reaction rate coefficients involving secondary radical types, corresponding to an arithmetic mean for the activation energies.

Table S6. Reaction mechanism for the autoxidation of poly(isobutylene); also given are the rate coefficients ((L mol^{-1}) s^{-1}) at 298 K; P = dead polymer chain, R* = polymer alkyl radical; RO* = polymer alkoxy radical; RO$_2^*$ = polymer alkyl peroxyl radical; end-groups according to Figure S3; *i* and *j* represent carbon number.

Reaction	***Reaction Equation***	k_f **((L mol^{-1})**	k_r **((L mol^{-}**	***Ref.***

		s^{-1})	^{1}) s^{-1})	
Initiation	$P_i \rightleftharpoons R_{prim,end,j} + R_{tert,end,i-j}$	1.0 10^{-10}	1.2 10^{2}	a, b
Propagation	$R_{prim,end,i} + O_2 \rightleftharpoons R_{prim,end,i}O_2{}^*$	4.0 10^{6}	0.0	1
	$R_{sec,mid,i} + O_2 \rightleftharpoons R_{sec,mid,i}O_2{}^*$	4.0 10^{6}	0.0	1
	$R_{tert,end,i} + O_2 \rightleftharpoons R_{tert,end,i}O_2{}^*$	4.0 10^{6}	0.0	1
	$R_{prim,end,i}O_2{}^* + R_{prim,end,j}O_2{}^* \rightleftharpoons R_{prim,end,i}O^* + R_{p}$	0.0	0.0	7
	$R_{prim,end,i}O_2{}^* + R_{sec,mid,j}O_2{}^* \rightleftharpoons R_{prim,end,i}O^* + R_{sec}$	0.0	0.0	7
	$R_{prim,end,i}O_2{}^* + R_{tert,end,j}O_2{}^* \rightleftharpoons R_{prim,end,i}O^* + R_{ter}$	0.0	0.0	7
	$R_{sec,mid,i}O_2{}^* + R_{sec,mid,j}O_2{}^* \rightleftharpoons R_{sec,mid,i}O^* + R_{sec,mi}$	0.0	0.0	7
	$R_{sec,mid,i}O_2{}^* + R_{tert,end,j}O_2{}^* \rightleftharpoons R_{sec,mid,i}O^* + R_{tert,e}$	0.0	0.0	7
	$R_{tert,end,i}O_2{}^* + R_{tert,end,j}O_2{}^* \rightleftharpoons R_{tert,end,i}O^* + R_{tert,}$	8.5 10^{3}	0.0	9
H-abstraction	$R_{prim,end,i}O_2{}^* + P_{secH,j} \rightleftharpoons R_{prim,end,i}OOH + R_{sec,mid,j}$	1.8 10^{-9}	3.6 10^{0}	d
	$R_{sec,mid,i}O_2{}^* + P_{secH,j} \rightleftharpoons R_{sec,mid,i}OOH + R_{sec,mid,j}$	2.7 10^{-8}	1.6 10^{-1}	c
	$R_{tert,end,i}O_2{}^* + P_{secH,j} \rightleftharpoons R_{tert,end,i}OOH + R_{sec,mid,j}$	4.0 10^{-7}	7.2 10^{1}	c
	$R_{prim,end,i} + P_{secH,j} \rightleftharpoons P_i + R_{sec,mid,j}$	8.0 10^{-7}	3.7 10^{-7}	d
	$R_{sec,mid,i} + P_{secH,j} \rightleftharpoons P_i + R_{sec,mid,j}$	1.2 10^{-4}	1.2 10^{-4}	c
	$R_{tert,end,i} + P_{secH,j} \rightleftharpoons P_i + R_{sec,mid,j}$	1.8 10^{-2}	3.9 10^{-2}	c
	$R_{prim,end,i}O^* + P_{secH,j} \rightleftharpoons R_{prim,end,i}OH + R_{sec,mid,j}$	3.7 10^{2}	4.7 10^{-4}	d
	$R_{sec,mid,i}O^* + P_{secH,j} \rightleftharpoons R_{sec,mid,i}OH + R_{sec,mid,j}$	3.8 10^{2}	9.2 10^{-5}	c
	$R_{tert,end,i}O^* + P_{secH,j} \rightleftharpoons R_{tert,end,i}OH + R_{sec,mid,j}$	3.8 10^{2}	1.8 10^{-5}	c
β-scission	$R_{sec,mid,i} \rightleftharpoons P_j + R_{tert,end,i-j}$	8.7 10^{-8}	0.0	3
Termination	$R_{prim,end,i}O_2{}^* + R_{prim,end,j} \rightleftharpoons R_{prim,end,i}OOR_{prim,end,j}$	1.2 10^{2}	0.0	b
	$R_{prim,end,i}O_2{}^* + R_{sec,mid,j} \rightleftharpoons R_{prim,end,i}OOR_{sec,mid,j}$	1.2 10^{2}	0.0	b
	$R_{prim,end,i}O_2{}^* + R_{tert,end,j} \rightleftharpoons R_{prim,end,i}OOR_{tert,end,j}$	1.2 10^{2}	0.0	b
	$R_{sec,mid,i}O_2{}^* + R_{prim,end,j} \rightleftharpoons R_{sec,mid,i}OOR_{prim,end,j}$	1.2 10^{2}	0.0	b
	$R_{sec,mid,i}O_2{}^* + R_{sec,mid,j} \rightleftharpoons R_{sec,mid,i}OOR_{sec,mid,j}$	1.2 10^{2}	0.0	b
	$R_{sec,mid,i}O_2{}^* + R_{tert,end,j} \rightleftharpoons R_{sec,mid,i}OOR_{tert,end,j}$	1.2 10^{2}	0.0	b
	$R_{tert,end,i}O_2{}^* + R_{prim,end,j} \rightleftharpoons R_{tert,end,i}OOR_{prim,end,j}$	1.2 10^{2}	0.0	b
	$R_{tert,end,i}O_2{}^* + R_{sec,mid,j} \rightleftharpoons R_{tert,end,i}OOR_{sec,mid,j}$	1.2 10^{2}	0.0	b
	$R_{tert,end,i}O_2{}^* + R_{tert,end,j} \rightleftharpoons R_{tert,end,i}OOR_{tert,end,j}$	1.2 10^{2}	0.0	b
	$R_{prim,end,i}O_2{}^* + R_{prim,end,j}O_2{}^* \rightleftharpoons R_{prim,end,i}C(O)H +$	1.6 10^{6}	0.0	8
	$R_{prim,end,i}O_2{}^* + R_{sec,mid,j}O_2{}^* \rightleftharpoons R_{prim,end,i}C(O)H +$	1.6 10^{6}	0.0	8
	$R_{prim,end,i}O_2{}^* + R_{tert,end,j}O_2{}^* \rightleftharpoons R_{prim,end,i}C(O)H +$	0.0	0.0	7
	$R_{sec,mid,i}O_2{}^* + R_{prim,end,j}O_2{}^* \rightleftharpoons R_{sec,mid,k}C(O)R_{sec,m}$	1.6 10^{6}	0.0	8
	$R_{sec,mid,i}O_2{}^* + R_{sec,mid,j}O_2{}^* \rightleftharpoons R_{sec,mid,k}C(O)R_{sec,mid}$	1.6 10^{6}	0.0	8
	$R_{sec,mid,i}O_2{}^* + R_{tert,end,j}O_2{}^* \rightleftharpoons R_{sec,mid,k}C(O)R_{sec,mi}$	0.0	0.0	7
	$R_{tert,end,i}O_2{}^* + R_{prim,end,j}O_2{}^* \rightleftharpoons R_{tert,end,i}C(O)H + R$	0.0	0.0	7
	$R_{tert,end,i}O_2{}^* + R_{sec,mid,j}O_2{}^* \rightleftharpoons R_{tert,end,i}C(O)H + R_{s}$	0.0	0.0	7
	$R_{tert,end,i}O_2{}^* + R_{tert,end,j}O_2{}^* \rightleftharpoons R_{tert,end,i}C(O)H + R$	0.0	0.0	7
Re-initiation	$R_{prim,end,i}OOR_{prim,end,j} \rightleftharpoons R_{prim,end,i}O^* + R_{prim,end,j}O$	8.4 10^{-13}	0.0	5
	$R_{prim,end,i}OOR_{sec,mid,j} \rightleftharpoons R_{prim,end,i}O^* + R_{sec,mid,j}O^*$	8.4 10^{-13}	0.0	5
	$R_{prim,end,i}OOR_{tert,end,j} \rightleftharpoons R_{prim,end,i}O^* + R_{tert,end,j}O^*$	1.0 10^{-13}	0.0	5

	$R_{sec,mid,i}OOR_{sec,mid,j} \rightleftharpoons R_{sec,mid,i}O^* + R_{sec,mid,j}O^*$	8.4 10^{-13}	0.0	5
	$R_{sec,mid,i}OOR_{tert,end,j} \rightleftharpoons R_{sec,mid,i}O^* + R_{tert,end,j}O^*$	1.0 10^{-13}	0.0	5
	$R_{tert,end,i}OOR_{tert,end,j} \rightleftharpoons R_{tert,end,i}O^* + R_{tert,end,j}O^*$	1.0 10^{-13}	0.0	5

[a]Forward rate coefficient: value chosen to reach realistic timescales (approximately one month is required to reduce the average chain length by a factor two); [b]Reverse rate coefficient: calculated using diffusion coefficient from Roland *et al.*[6] and Smoluchowski relationship (r = 4.7 10^{-10} m); [c]Calculated in this work; see Table S1; [d]H abstraction rate coefficients for primary radicals are calculated based on results for secondary and tertiary radicals (Table S1) assuming a geometric average for reaction rate coefficients involving secondary radical types, corresponding to an arithmetic mean for the activation energies.

S4. Additional simulation results for autoxidation modelling

S4.1. Confirmation of chain reaction mechanism

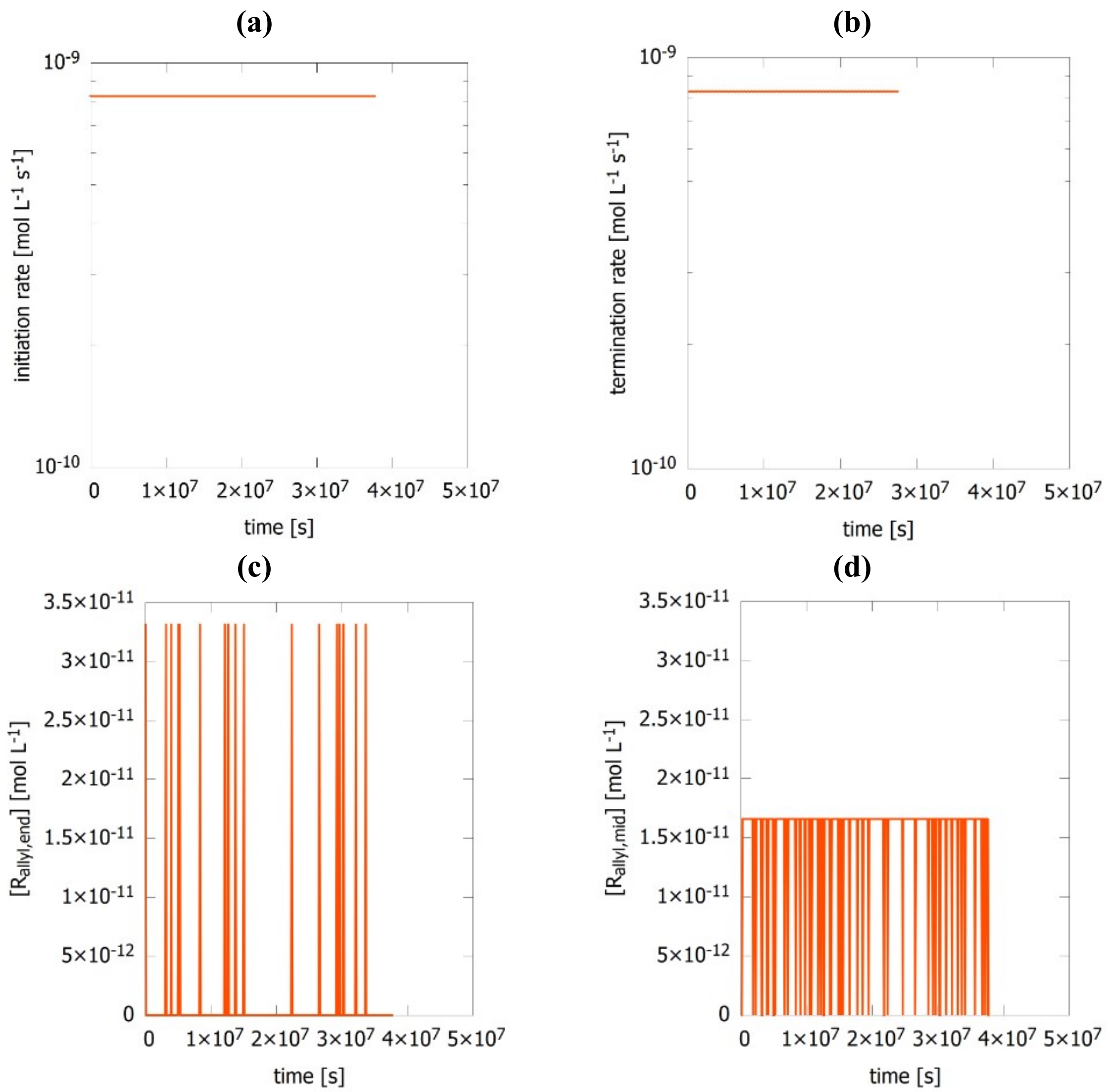
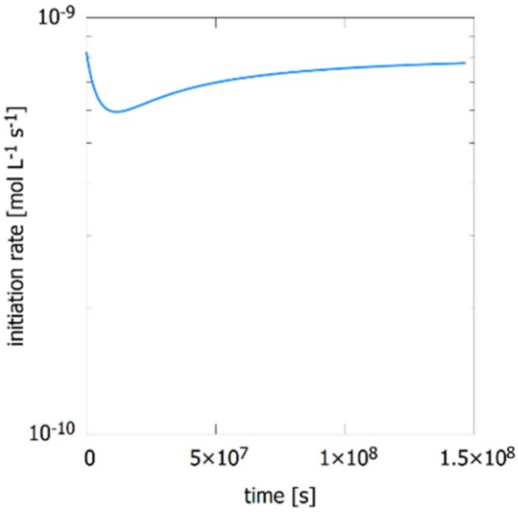
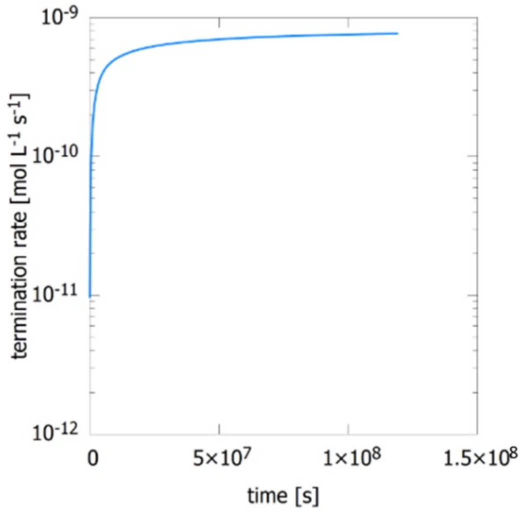


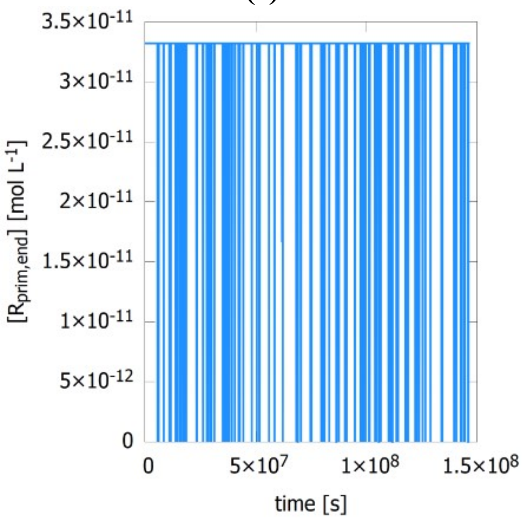
Figure S5. Chain reaction mechanism for poly(butadiene): **(a)** total initiation rate (mol L^{-1} s^{-1}), **(b)** total termination rate (mol L^{-1} s^{-1}), **(c)** concentration of $R_{allyl,end}$ (mol L^{-1}), and **(d)** concentration of $R_{allyl,mid}$ (mol L^{-1}) as a function of time (s).

(a) **(b)**





(c) **(d)**



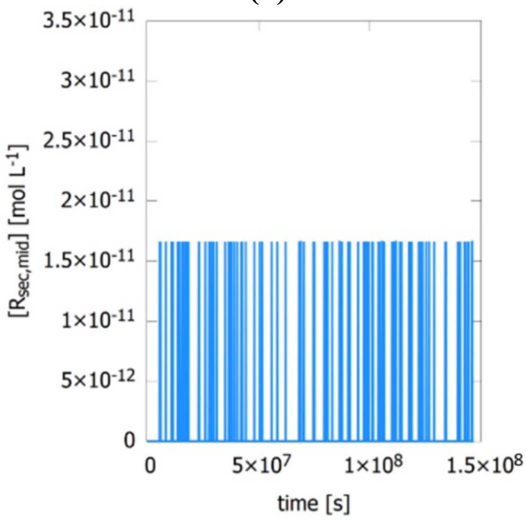
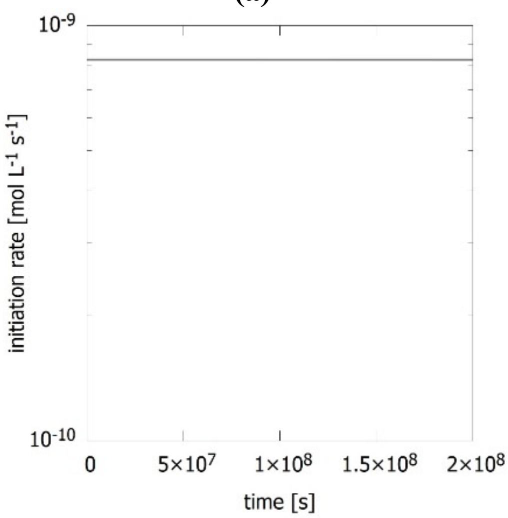
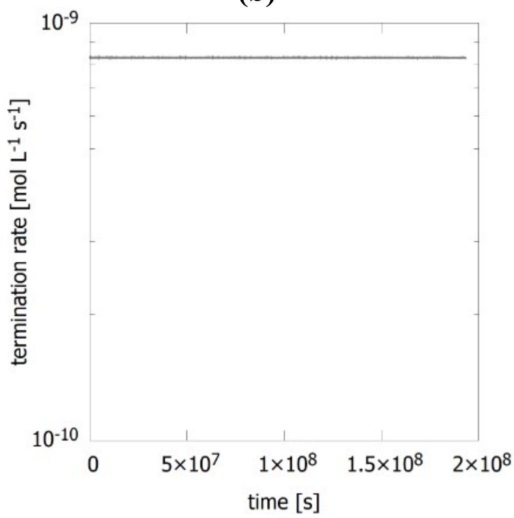


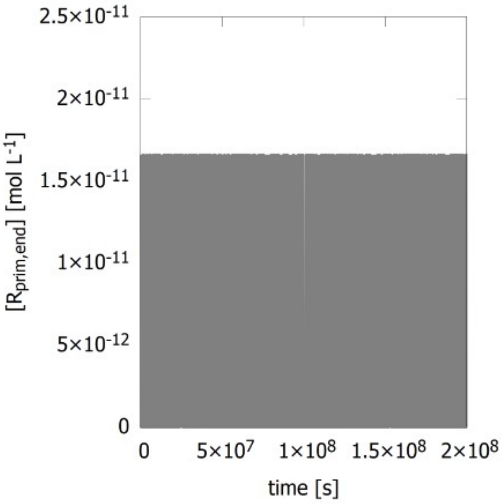
Figure S6. Chain reaction mechanism for poly(ethylene): **(a)** total initiation rate (mol L^{-1} s^{-1}), **(b)** total termination rate (mol L^{-1} s^{-1}), **(c)** concentration of $R_{prim,end}$ (mol L^{-1}), and **(d)** concentration of $R_{sec,mid}$ (mol L^{-1}) as a function of time (s).

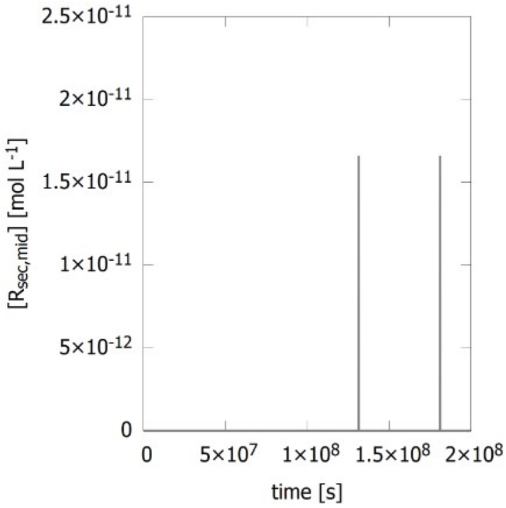
(a) **(b)**





(c) **(d)**





(e)

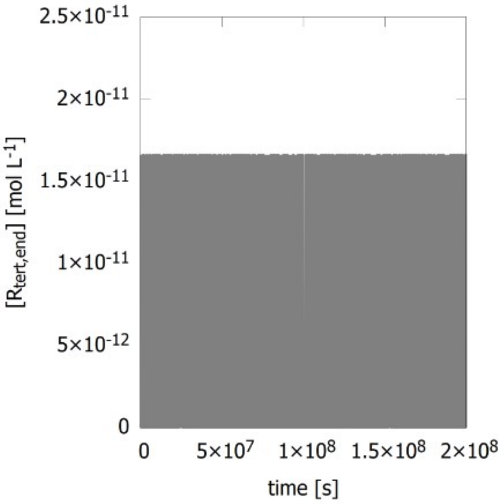
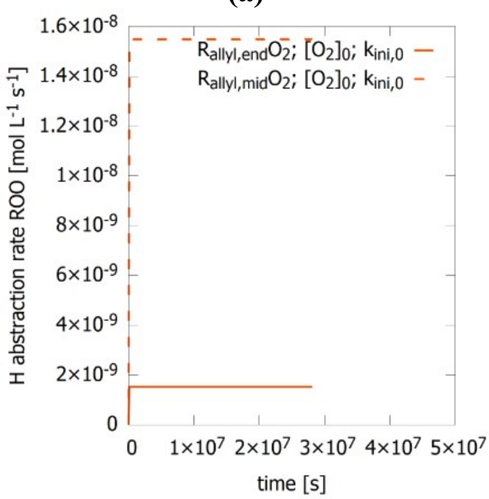


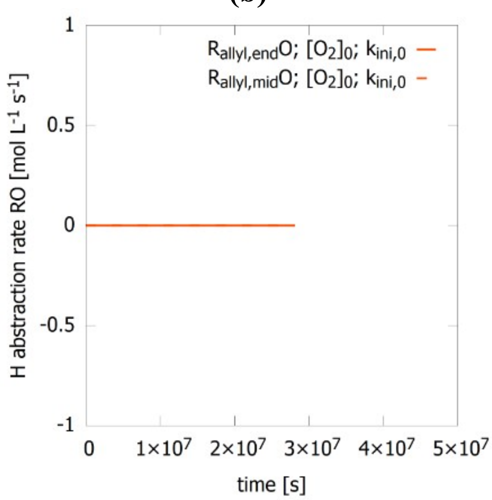
Figure S7. Chain reaction mechanism for poly(isobutylene): **(a)** total initiation rate (mol L^{-1} s^{-1}), **(b)** total termination rate (mol L^{-1} s^{-1}), concentration of **(c)** $R_{pim,end}$ (mol L^{-1}), **(d)** $R_{sec,mid}$ (mol L^{-1}), and **(e)** $R_{tert,end}$ (mol L^{-1}) as a function of time (s).

S4.2. Additional simulation results for poly(butadiene)

(a)



(b)



(c)

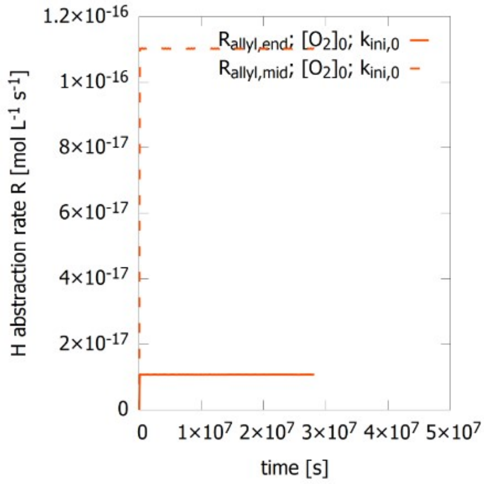


Figure S8. Hydrogen abstraction reaction rates for poly(isobutylene) (mol L^{-1} s^{-1}) for: **(a)** alkylperoxyl radicals $RO_2^{\bullet}$, **(b)** alkoxyl radicals $RO^{\bullet}$ and **(c)** alkyl radicals $R^{\bullet}$ as a function of time (s) for allylic end radicals (full lines) and allylic midchain radicals (dashed lines).

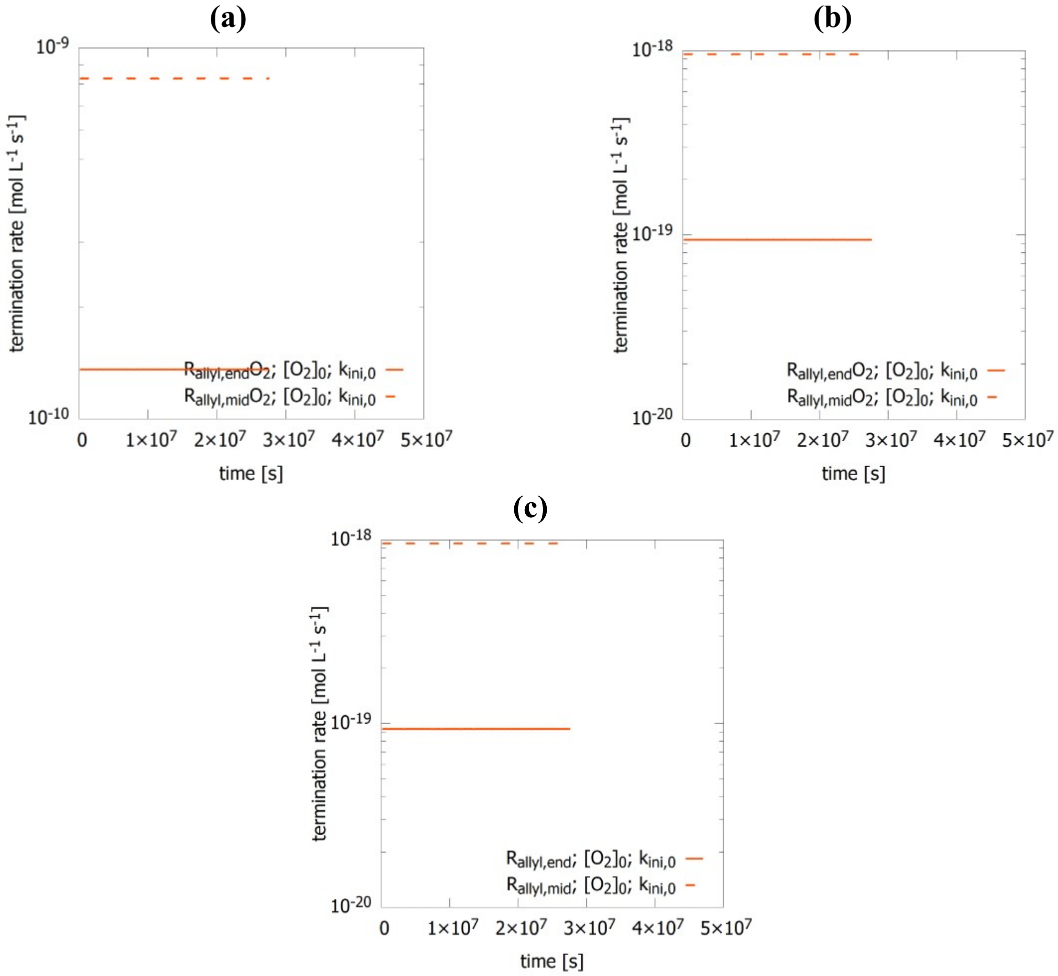


Figure S9. Termination reaction rates for poly(isobutylene) (mol L^{-1} s^{-1}) for: **(a)** termination of two alkylperoxyl radicals ($RO_2^{\bullet}$ + $RO_2^{\bullet}$), **(b)** and **(c)** termination of alkylperoxyl radical and alkyl radical ($RO_2^{\bullet}$ + $R^{\bullet}$); reaction partner under consideration is specified in legend; reaction partner related to allylic end radicals (full lines) and allylic midchain radicals (dashed lines); termination reaction rates for alkoxyl radicals not shown as equal to 0.

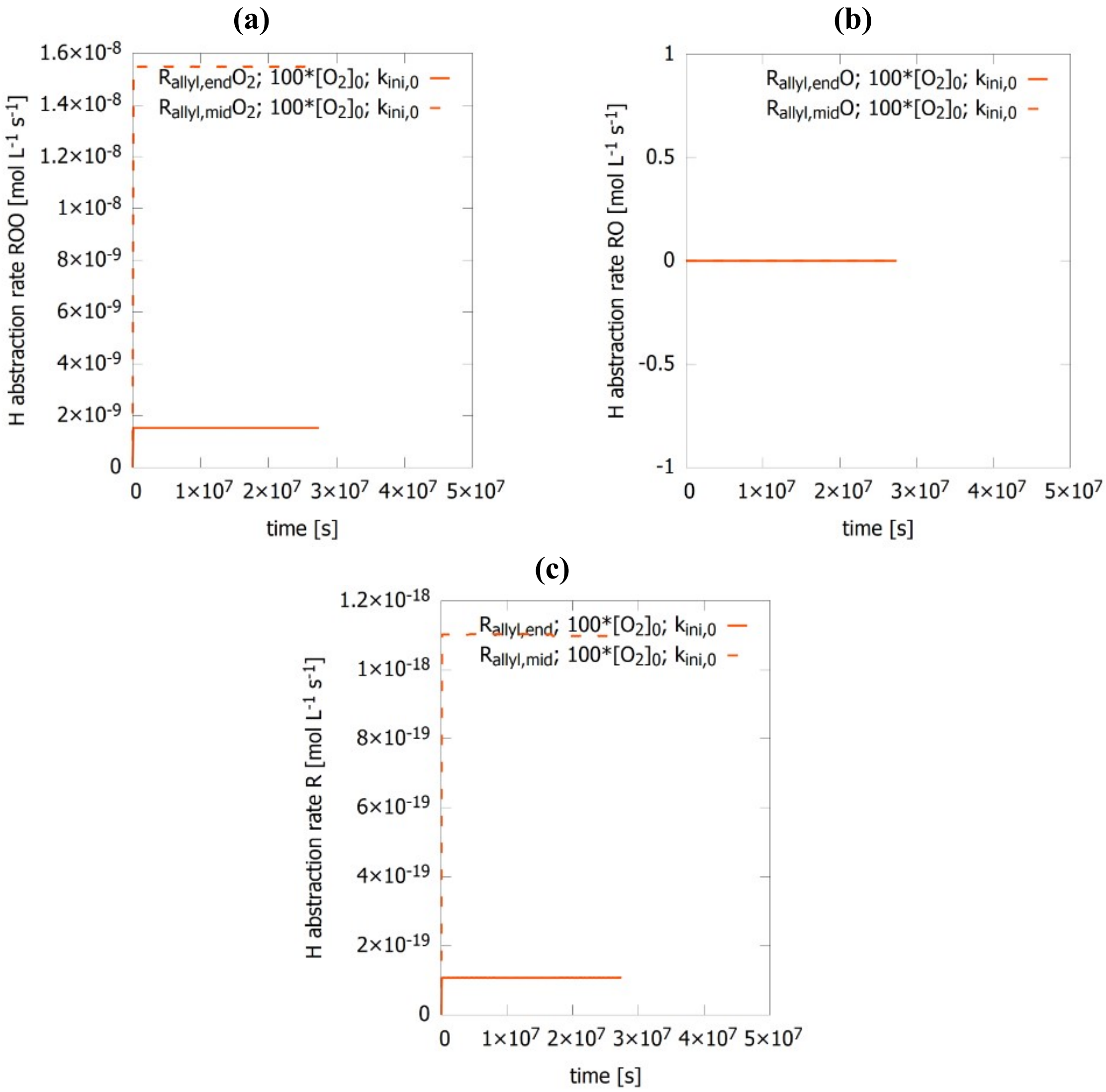
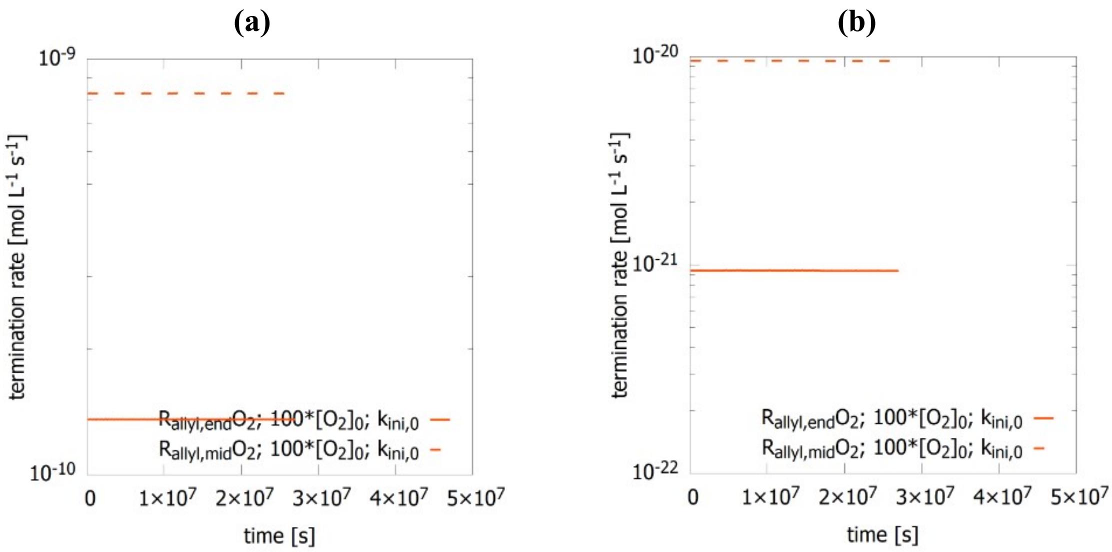


Figure S10. Hydrogen abstraction reaction rates for poly(isobutylene) with a higher oxygen concentration ($[O_2] = 100[O_2]_0$) (mol L^{-1} s^{-1}) for: **(a)** alkylperoxyl radicals $RO_2^{\bullet}$, **(b)** alkoxyl radicals $RO^{\bullet}$ and **(c)** alkyl radicals $R^{\bullet}$ as a function of time (s) for allylic end radicals (full lines) and allylic midchain radicals (dashed lines).



(c)

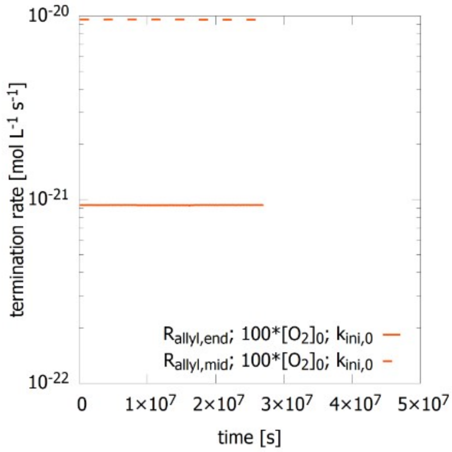


Figure S11. Termination reaction rates for poly(isobutylene) with a higher oxygen concentration ($[O_2] = 100[O_2]_0$) (mol L^{-1} s^{-1}) for: **(a)** termination between two alkylperoxyl radicals ($RO_2^• + RO_2^•$), **(b)** and **(c)** termination between alkylperoxyl radical and alkyl radical ($RO_2^• + R^•$); reaction partner under consideration is specified in legend; reaction partner related to allylic end radicals (full lines) and allylic midchain radicals (dashed lines); termination reaction rates for alkoxyl radicals are not shown as they are equal to 0.

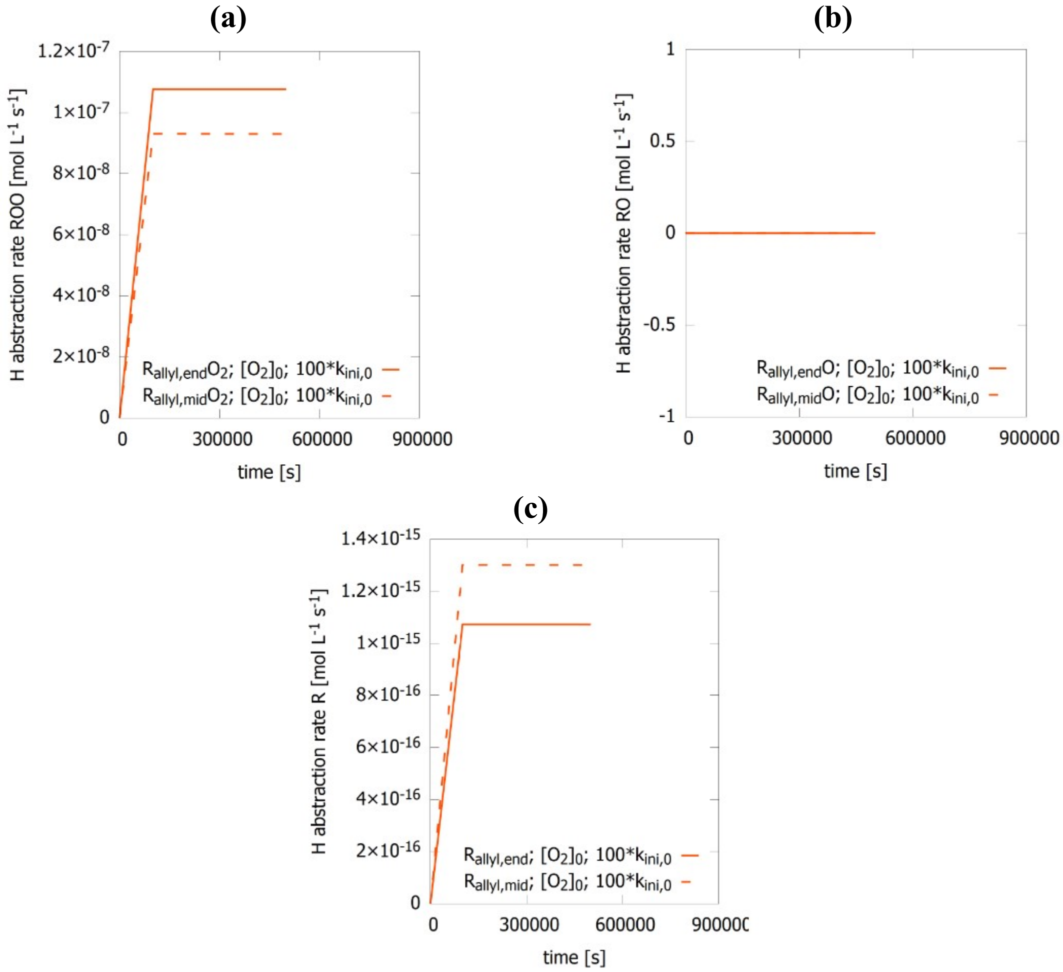


Figure S12. Hydrogen abstraction reaction rates for poly(isobutylene) with a higher initiation rate coefficient ($k_{ini} = 100k_{ini}$) (mol L^{-1} s^{-1}) for: **(a)** alkylperoxyl radicals $RO_2^•$, **(b)** alkoxyl radicals $RO^•$ and **(c)** alkyl radicals $R^•$ as a function of time (s) for allylic end radicals (full lines) and allylic midchain radicals (dashed lines).

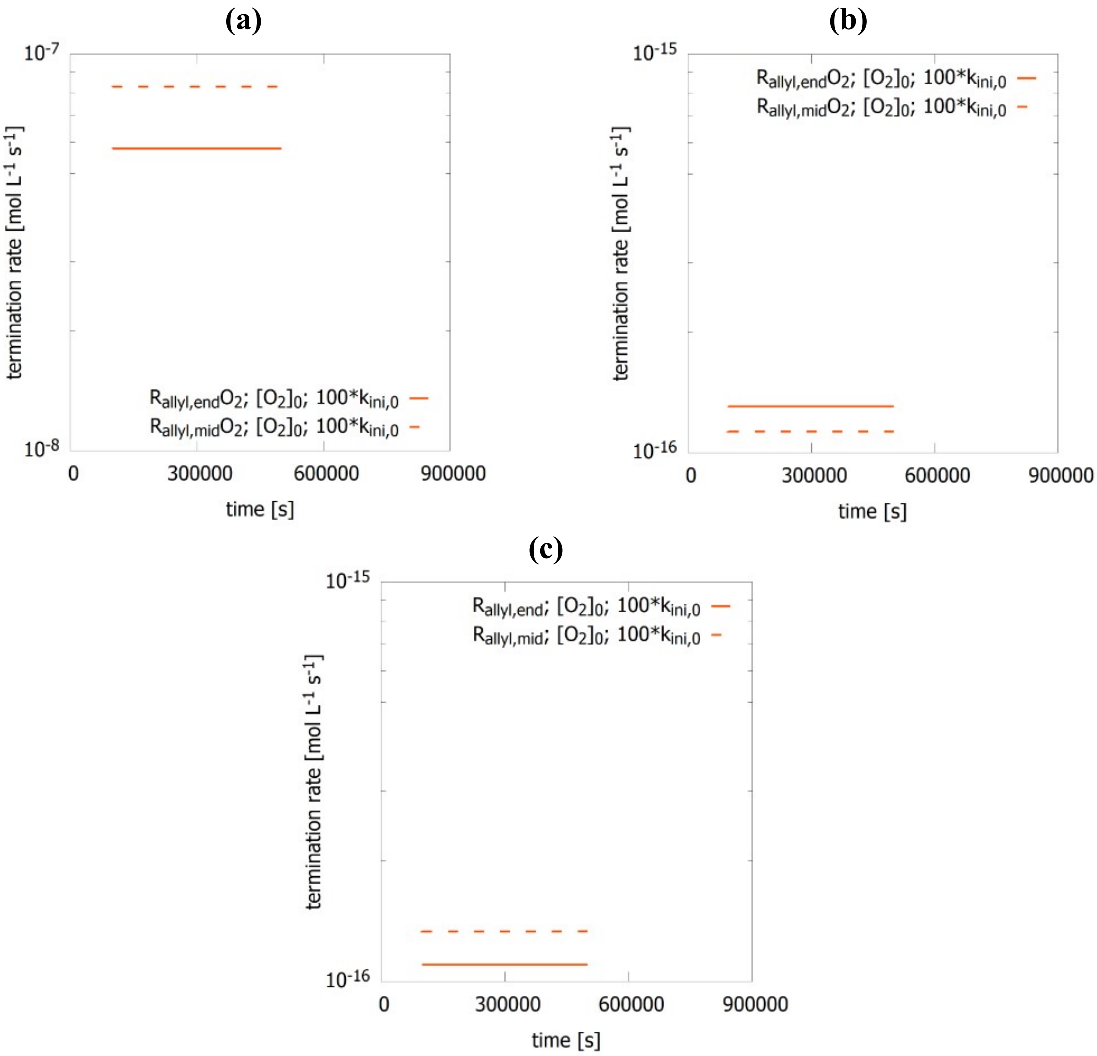


Figure S13. Termination reaction rates for poly(isobutylene) with a higher initiation rate coefficient (k_{ini} = 100k_{ini}) (mol L^{-1} s^{-1}) for: **(a)** termination between two alkylperoxyl radicals ($RO_2^•$ + $RO_2^•$), **(b)** and **(c)** termination between alkylperoxyl radical and alkyl radical ($RO_2^•$ + $R^•$); reaction partner under consideration is specified in legend; reaction partner related to allylic end radicals (full lines) and allylic midchain radicals (dashed lines); termination reaction rates for alkoxyl radicals are not shown as they are equal to 0.

Table S7. Summary of *k*MC model output related to reaction rates (mol L^{-1} s^{-1}) of competitive reactions for poly(butadiene) with a higher O_2 concentration ($[O_2]$ = 100$[O_2]_0$); reaction rates as a function of time are given in Figure S10 and S11; red: lowest reaction rates; green: largest reaction rates; values indicated in black are set equal to 0.

1st reaction partner	***Propagation***				***Termination***		
	$RO_2^•$ + P	$RO^•$ + P	$R^•$ + P	$RO_2^•$ + $RO_2^•$	$RO_2^•$ + $RO_2^•$	$RO_2^•$ + $R^•$	$R^•$ + $RO_2^•$
$\mathbf{R_{allyl,end}}$	2.0 10^{-9}	0.0	1.0 10^{-19}	0.0	1.5 10^{-10}	1.0 10^{-21}	1.0 10^{-21}
$\mathbf{R_{allyl,mid}}$	1.5 10^{-8}	0.0	1.0 10^{-18}	0.0	7.0 10^{-9}	1.0 10^{-20}	1.0 10^{-20}

Table S8. Summary of *k*MC model output related to reaction rates (mol L^{-1} s^{-1}) of competitive reactions for poly(butadiene) with a higher initiation rate coefficient (k_{ini} = 100k_{ini}); reaction rates as a function of time are given in Figure S12 and S13; red: lowest reaction rates; green: largest reaction rates; values indicated in black are set equal to 0.

1st reaction partner	***Propagation***				***Termination***		
	$RO_2^• + P$	$RO^• + P$	$R^• + P$	$RO_2^• + RO_2^•$	$RO_2^• + RO_2^•$	$RO_2^• + R^•$	$R^• + RO_2^•$
$\mathbf{R_{allyl,end}}$	1.0 10^{-7}	0.0	1.0 10^{-15}	0.0	5.0 10^{-8}	1.0 10^{-16}	1.0 10^{-16}
$\mathbf{R_{allyl,mid}}$	9.0 10^{-8}	0.0	1.3 10^{-15}	0.0	8.0 10^{-8}	1.0 10^{-16}	1.0 10^{-16}

S4.3. Additional simulation results for poly(ethylene)

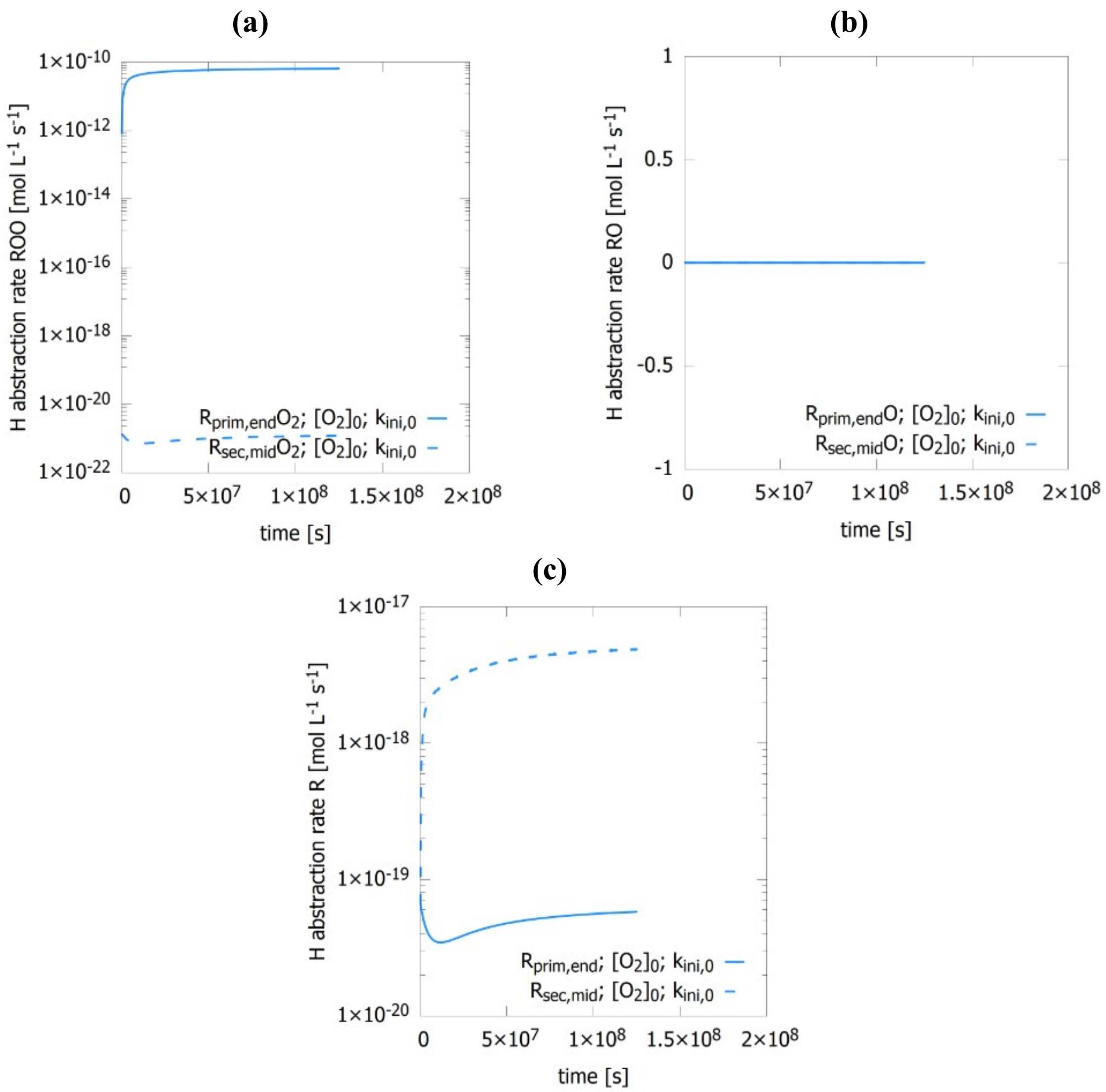


Figure S14. Hydrogen abstraction reaction rates for poly(ethylene) (mol L^{-1} s^{-1}) for: **(a)** alkylperoxyl radicals $RO_2^•$, **(b)** alkoxyl radicals $RO^•$ and **(c)** alkyl radicals $R^•$ as a function of time (s) for primary end- (full lines) and secondary midchain radicals (dashed lines).

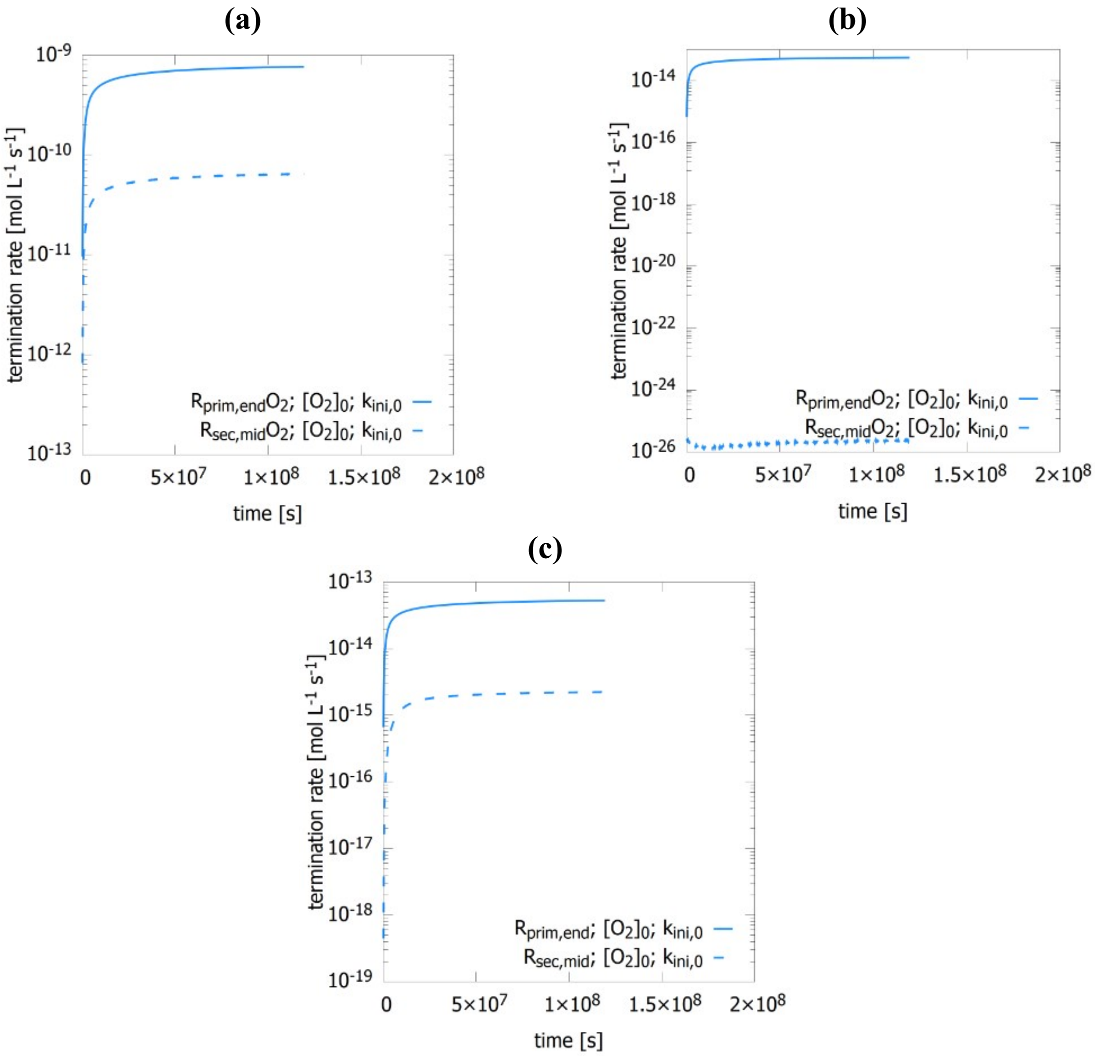
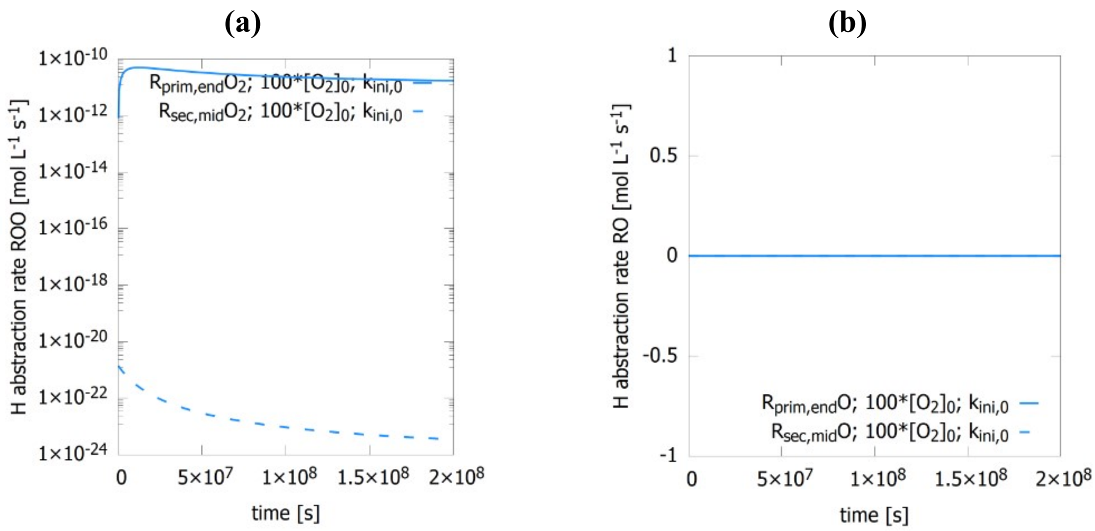


Figure S15. Termination reaction rates for poly(ethylene) (mol L^{-1} s^{-1}) for: **(a)** termination between two alkylperoxyl radicals ($RO_2^{\bullet} + RO_2^{\bullet}$), **(b)** and **(c)** termination between alkylperoxyl radical and alkyl radical ($RO_2^{\bullet} + R^{\bullet}$); reaction partner under consideration is specified in legend; reaction partner related to primary end radicals (full lines) and secondary midchain radicals (dashed lines); termination reaction rates for alkoxyl radicals are not shown as they are equal to 0.



(c)

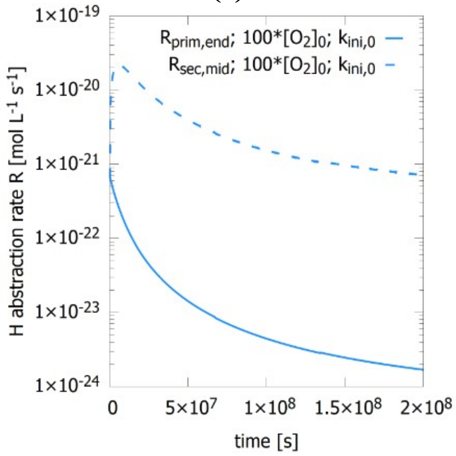
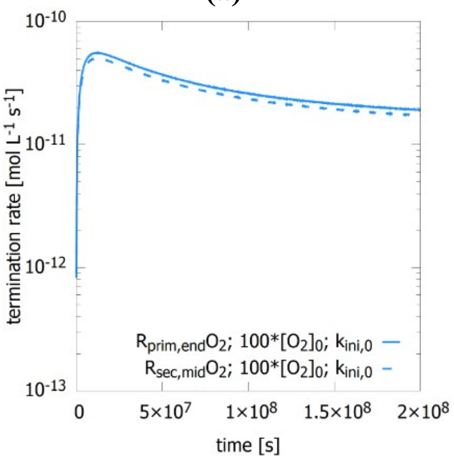
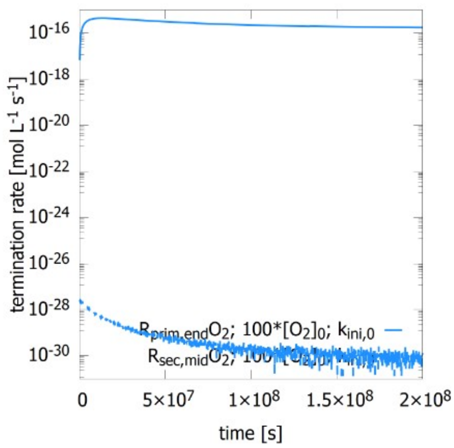


Figure S16. Hydrogen abstraction reaction rates for poly(ethylene) with a higher oxygen concentration ($[O_2] = 100[O_2]_0$) (mol L^{-1} s^{-1}) for: **(a)** alkylperoxyl radicals $RO_2^{\bullet}$, **(b)** alkoxyl radicals $RO^{\bullet}$ and **(c)** alkyl radicals $R^{\bullet}$ as a function of time (s) for primary end radicals (full lines) and secondary midchain radicals (dashed lines).

(a)



(b)



(c)

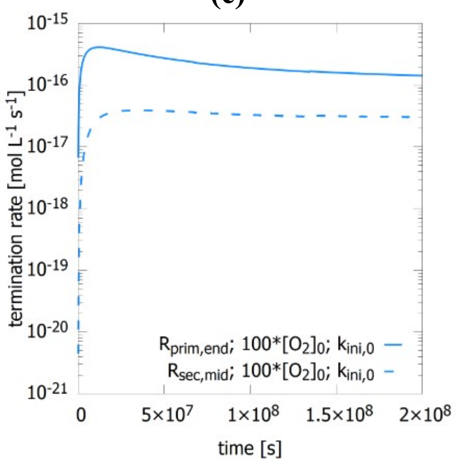


Figure S17. Reaction rates for poly(ethylene) with a higher O_2 concentration ($[O_2] = 100[O_2]_0$) (mol L^{-1} s^{-1}) for: **(a)** termination between two alkylperoxyl radicals ($RO_2^{\bullet}$ + $RO_2^{\bullet}$), **(b)** and **(c)** termination between alkylperoxyl radical and alkyl radical ($RO_2^{\bullet}$ + $R^{\bullet}$); reaction partner under consideration is specified in legend; reaction partner related to primary end- (full lines) and secondary midchain radicals (dashed lines); termination reaction rates for alkoxyl radicals not shown as equal to 0.

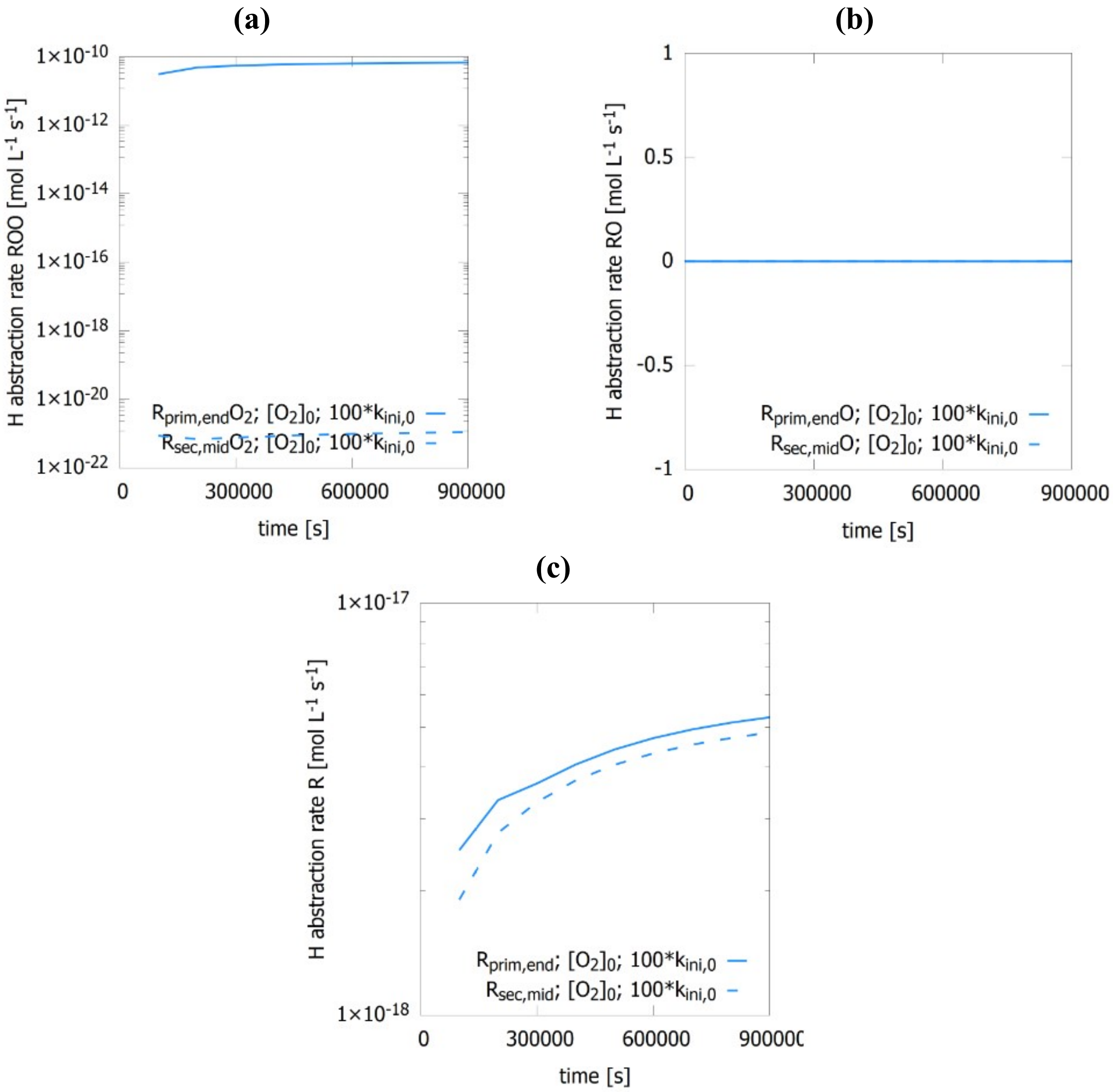
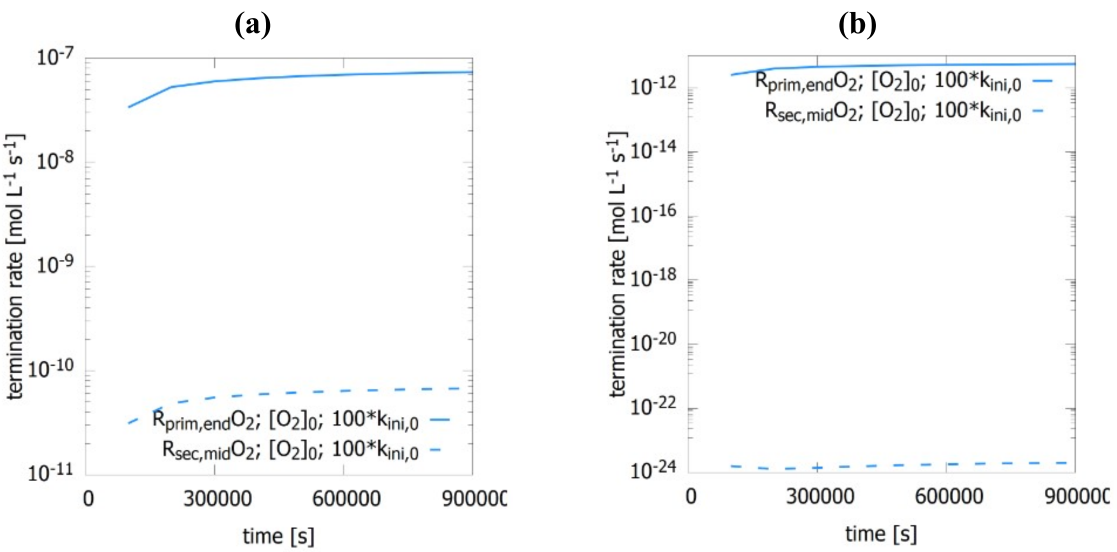


Figure S18. Hydrogen abstraction reaction rates for poly(ethylene) with a higher initiation rate coefficient (k_{ini} = 100k_{ini}) (mol L^{-1} s^{-1}) for: **(a)** alkylperoxyl radicals $RO_2^{\bullet}$, **(b)** alkoxyl radicals $RO^{\bullet}$ and **(c)** alkyl radicals $R^{\bullet}$ as a function of time (s) for primary end radicals (full lines) and secondary midchain radicals (dashed lines).



(c)

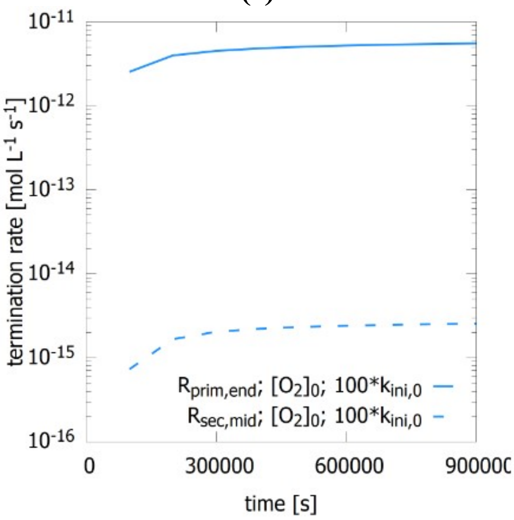


Figure S19. Termination reaction rates for poly(ethylene) with a higher initiation rate coefficient (k_{ini} = 100k_{ini}) (mol L^{-1} s^{-1}) for: **(a)** termination between two alkylperoxyl radicals ($RO_2^•$ + $RO_2^•$), **(b)** and **(c)** termination between alkylperoxyl radical and alkyl radical ($RO_2^•$ + $R^•$); reaction partner under consideration is specified in legend; reaction partner related to primary end radicals (full lines) and secondary midchain radicals (dashed lines); termination reaction rates for alkoxyl radicals are not shown as they are equal to 0.

Table S9. Summary of *k*MC model output related to reaction rates (mol L^{-1} s^{-1}) of competitive reactions for poly(ethylene) with a higher O_2 concentration ($[O_2]$ = 100$[O_2]_0$); reaction rates as a function of time are given in Figure S16 and S17; red: lowest reaction rates; green: largest reaction rates; values indicated in black are set equal to 0.

1st reaction partner	***Propagation***				***Termination***		
	$RO_2^•$ + P	$RO^•$ + P	$R^•$ + P	$RO_2^•$ + $RO_2^•$	$RO_2^•$ + $RO_2^•$	$RO_2^•$ + $R^•$	$R^•$ + $RO_2^•$
$\mathbf{R_{prim,end}}$	3.0 10^{-12}	0.0	6.5 10^{-23}	0.0	5.0 10^{-11}	1.0 10^{-16}	1.0 10^{-16}
$\mathbf{R_{sec,mid}}$	1.0 10^{-23}	0.0	6.5 10^{-21}	0.0	5.0 10^{-11}	1.0 10^{-30}	2.0 10^{-17}

Table S10. Summary of *k*MC model output related to reaction rates (mol L^{-1} s^{-1}) of competitive reactions for poly(ethylene) with a higher initiation rate coefficient (k_{ini} = 100k_{ini}); reaction rates as a function of time are given in Figure S18 and S19; red: lowest reaction rates; green: largest reaction rates; values indicated in black are set equal to 0.

1st reaction partner	***Propagation***				***Termination***		
	$RO_2^•$ + P	$RO^•$ + P	$R^•$ + P	$RO_2^•$ + $RO_2^•$	$RO_2^•$ + $RO_2^•$	$RO_2^•$ + $R^•$	$R^•$ + $RO_2^•$
$\mathbf{R_{prim,end}}$	5.0 10^{-11}	0.0	5.0 10^{-18}	0.0	7.5 10^{-8}	1.0 10^{-12}	5.0 10^{-12}
$\mathbf{R_{sec,mid}}$	1.0 10^{-21}	0.0	5.0 10^{-18}	0.0	7.0 10^{-11}	1.0 10^{-24}	2.0 10^{-15}

S4.4. Additional simulation results for poly(isobutylene)

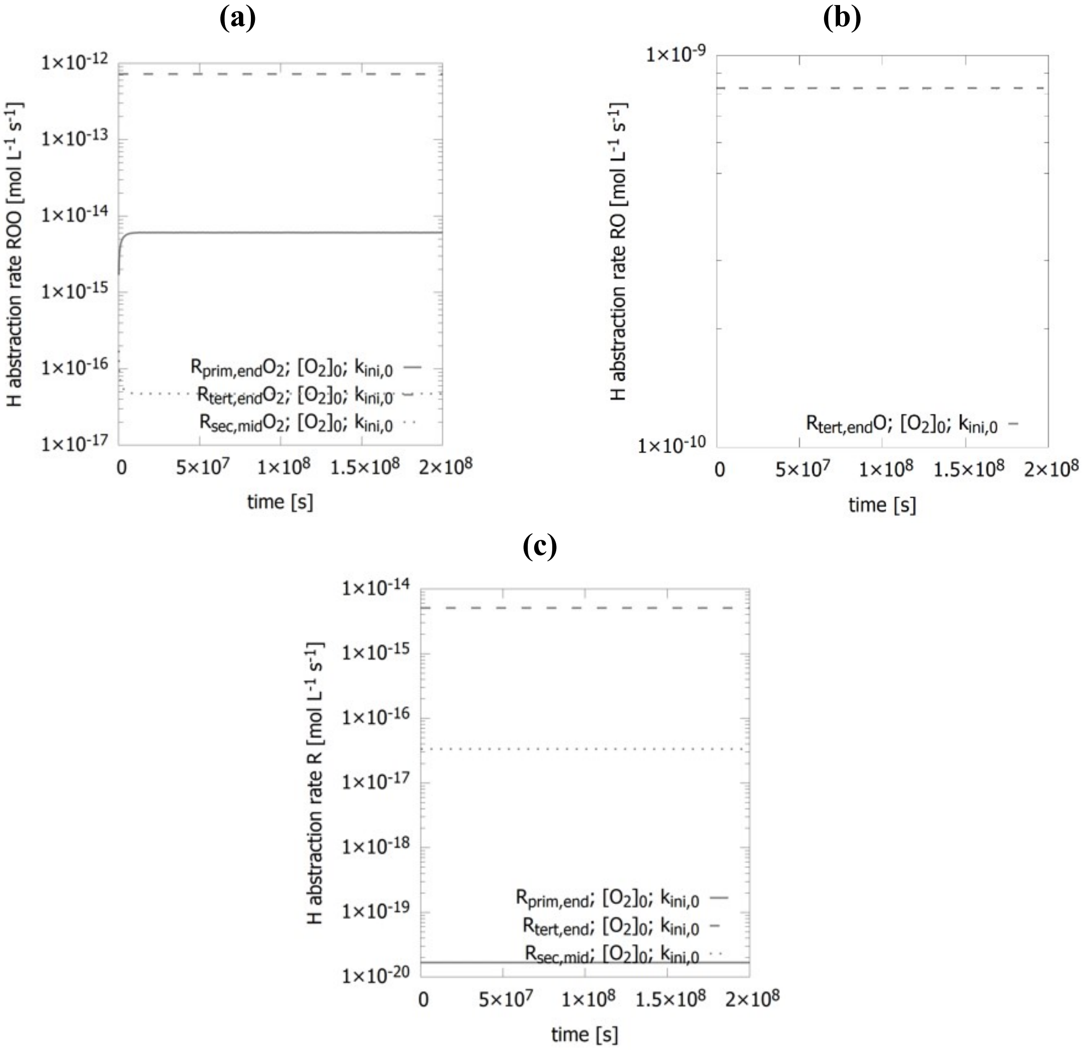
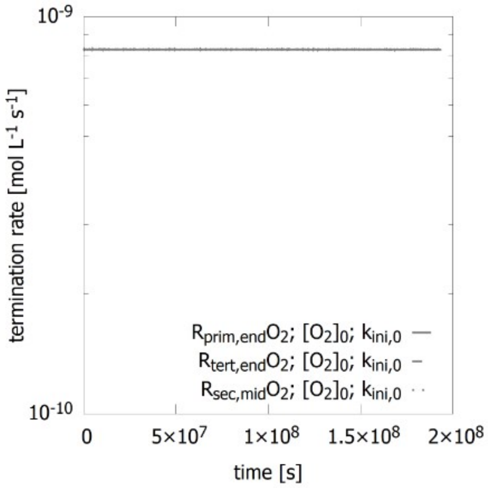
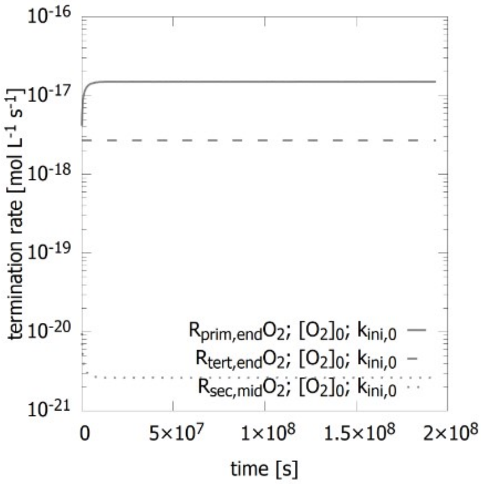


Figure S20. Hydrogen abstraction reaction rates for poly(isobutylene) (mol L^{-1} s^{-1}) for: **(a)** alkylperoxyl radicals $RO_2^{\bullet}$, **(b)** alkoxyl radicals $RO^{\bullet}$ and **(c)** alkyl radicals $R^{\bullet}$ as a function of time (s) for primary end radicals (full lines), tertiary end radicals (dashed lines) and secondary midchain radicals (dotted lines).

(a) **(b)**





(c)

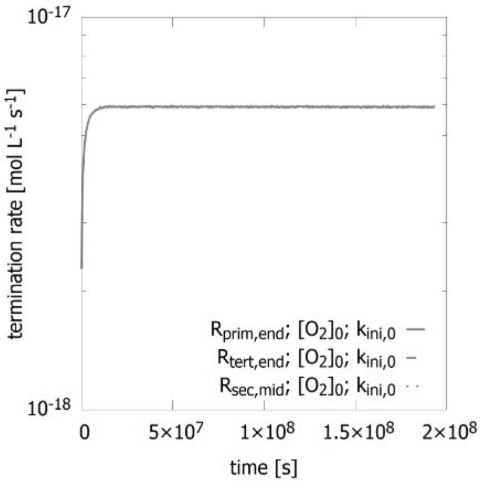


Figure S21. Termination reaction rates for poly(isobutylene) (mol L^{-1} s^{-1}) for: **(a)** termination between two alkylperoxyl radicals ($RO_2^{\bullet} + RO_2^{\bullet}$), **(b)** and **(c)** termination between alkylperoxyl radical and alkyl radical ($RO_2^{\bullet} + R^{\bullet}$); reaction partner under consideration is specified in legend; reaction partner related to primary end radicals (full lines) and secondary midchain radicals (dashed lines); termination reaction rates for alkoxyl radicals are not shown as they are equal to 0.

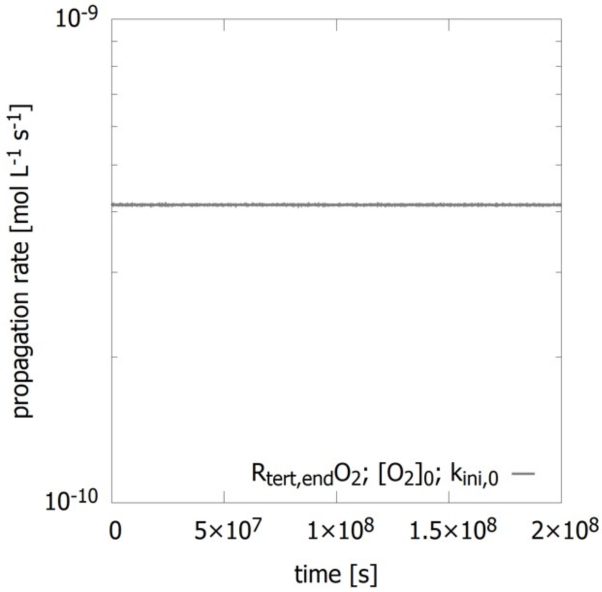


Figure S22. Propagation reaction rates for poly(isobutylene) (mol L^{-1} s^{-1}) for reaction between two tertiary end alkylperoxyl radicals ($R_{tert,end}O_2^{\bullet}$ + $R_{tert,end}O_2^{\bullet}$) with the formation of two alkoxyl radicals ($R_{tert,end}O^{\bullet}$).

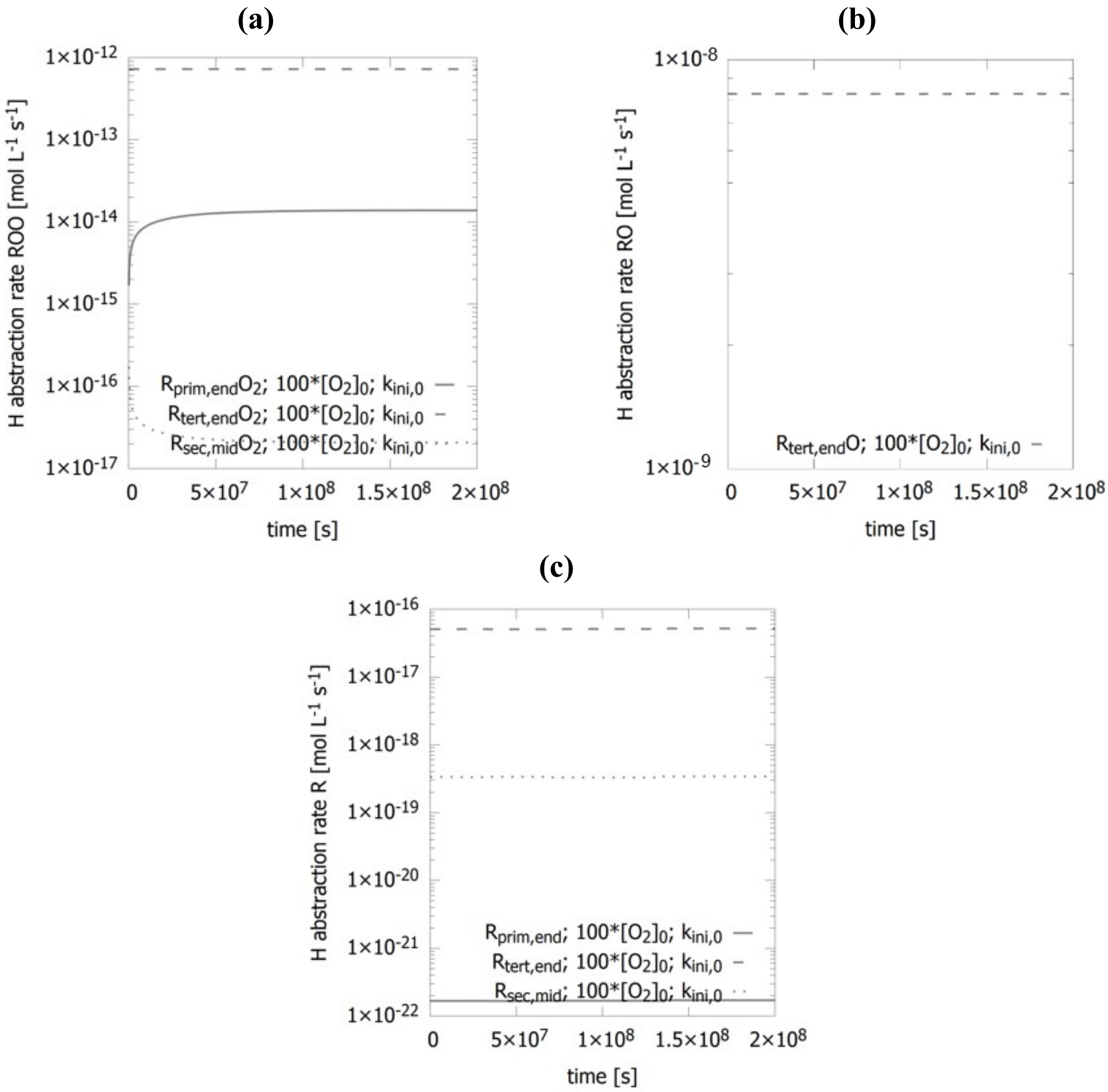
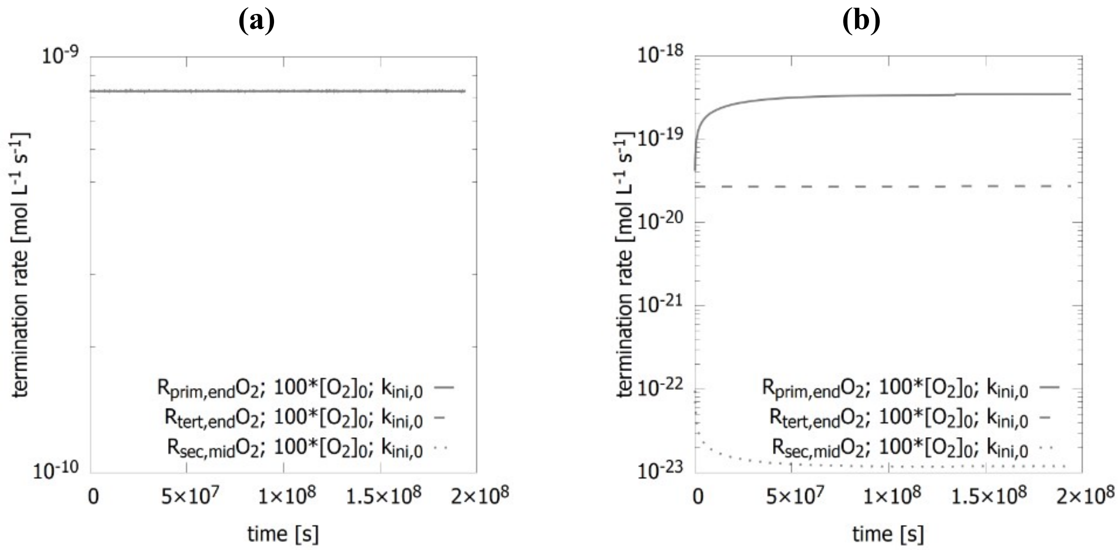


Figure S23. Hydrogen abstraction reaction rates for poly(isobutylene) with a higher oxygen concentration ($[O_2] = 100[O_2]_0$) (mol L^{-1} s^{-1}) for: **(a)** alkylperoxyl radicals $RO_2^{\bullet}$, **(b)** alkoxyl radicals $RO^{\bullet}$ and **(c)** alkyl radicals $R^{\bullet}$ as a function of time (s) for primary end radicals (full lines), tertiary end radicals (dashed lines) and secondary midchain radicals (dotted lines).



(c)

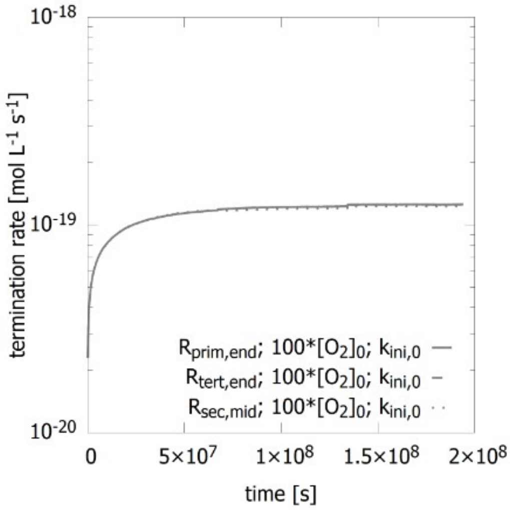


Figure S24. Termination reaction rates for poly(isobutylene) with a higher oxygen concentration ($[O_2] = 100[O_2]_0$) (mol L^{-1} s^{-1}) for: **(a)** termination between two alkylperoxyl radicals ($RO_2^{\bullet} + RO_2^{\bullet}$), **(b)** and **(c)** termination between alkylperoxyl radical and alkyl radical ($RO_2^{\bullet} + R^{\bullet}$); reaction partner under consideration is specified in legend; reaction partner related to primary end radicals (full lines) and secondary midchain radicals (dashed lines); termination reaction rates for alkoxyl radicals are not shown as they are equal to 0.

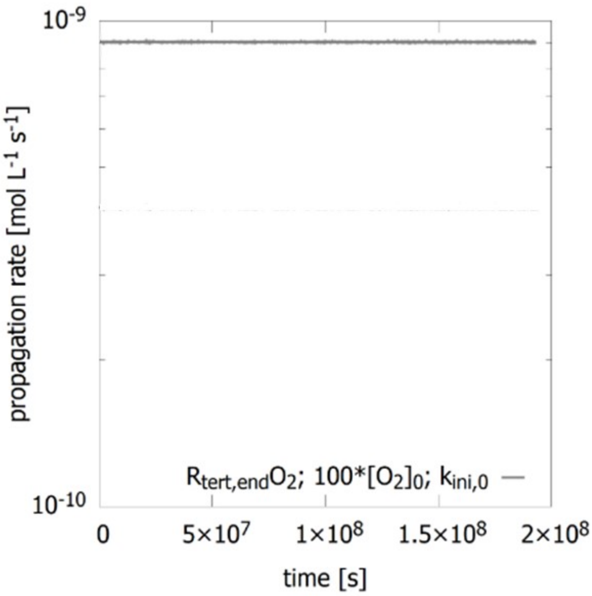


Figure S25. Propagation reaction rates for poly(isobutylene) with a higher oxygen concentration ($[O_2] = 100[O_2]_0$) (mol L^{-1} s^{-1}) for reaction between two tertiary end alkylperoxyl radicals ($R_{tert,end}O_2^{\bullet} + R_{tert,end}O_2^{\bullet}$) with the formation of two alkoxyl radicals ($R_{tert,end}O^{\bullet}$).

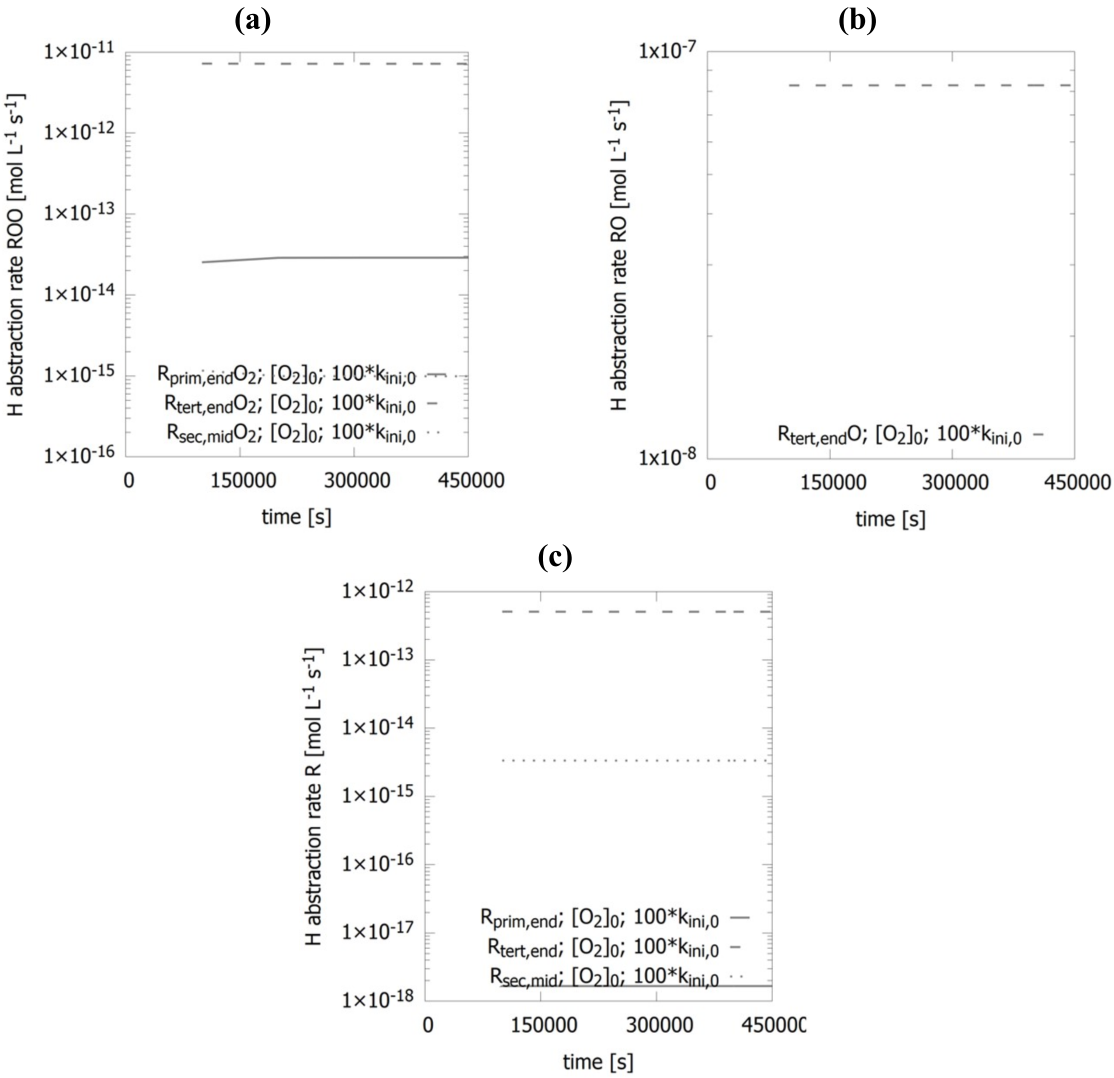
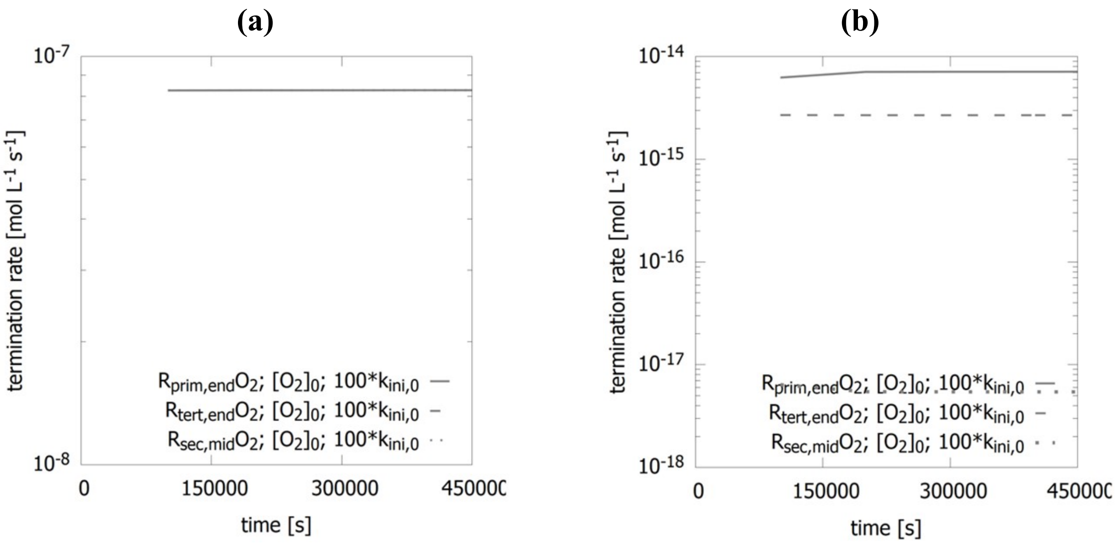


Figure S26. Hydrogen abstraction reaction rates for poly(isobutylene) with a higher initiation rate coefficient (k_{ini} = 100k_{ini}) (mol L^{-1} s^{-1}) for: **(a)** alkylperoxyl radicals $RO_2^{\bullet}$, **(b)** alkoxyl radicals $RO^{\bullet}$ and **(c)** alkyl radicals $R^{\bullet}$ as a function of time (s) for primary end radicals (full lines), tertiary end radicals (dashed lines) and secondary midchain radicals (dotted lines).



(c)

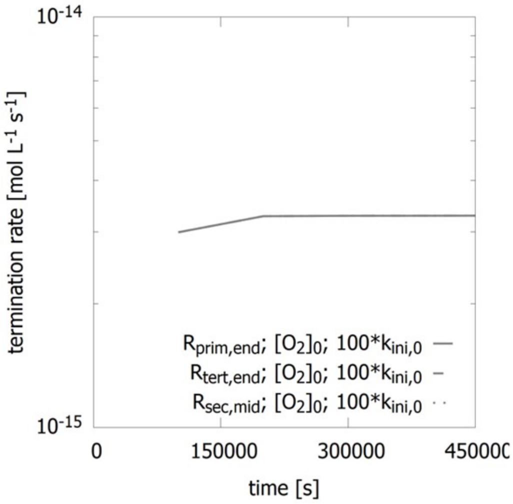


Figure S27. Termination reaction rates for poly(isobutylene) with a higher initiation rate coefficient (k_{ini} = $100k_{ini}$) (mol L^{-1} s^{-1}) for: **(a)** termination between two alkylperoxyl radicals ($RO_2^{\bullet}$ + $RO_2^{\bullet}$), **(b)** and **(c)** termination between alkylperoxyl radical and alkyl radical ($RO_2^{\bullet}$ + $R^{\bullet}$); reaction partner under consideration is specified in legend; reaction partner related to primary end radicals (full lines) and secondary midchain radicals (dashed lines); termination reaction rates for alkoxyl radicals are not shown as they are equal to 0.

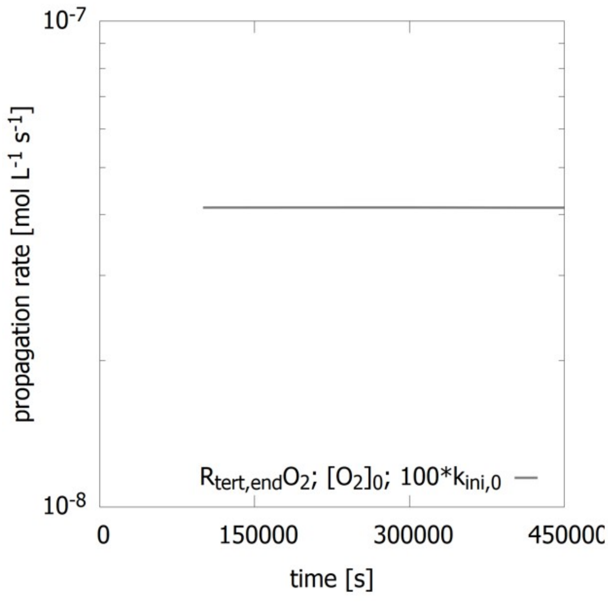


Figure S28. Propagation reaction rates for poly(isobutylene) with a higher initiation rate coefficient (k_{ini} = $100k_{ini}$) (mol L^{-1} s^{-1}) for reaction between two tertiary end alkylperoxyl radicals ($R_{tert,end}O_2^{\bullet}$ + $R_{tert,end}O_2^{\bullet}$) with the formation of two alkoxyl radicals ($R_{tert,end}O^{\bullet}$).

Table S11. Summary of *k*MC model output related to reaction rates (mol L^{-1} s^{-1}) of competitive reactions for poly(isobutylene) with a higher oxygen concentration ($[O_2] = 100[O_2]_0$); reaction rates as a function of time are given in Figure S23 to S25; red: lowest reaction rates; green: largest reaction rates; values indicated in black are set equal to 0.

1st reaction partner	***Propagation***				***Termination***		
	$RO_2^{\bullet} + P$	$RO^{\bullet} + P$	$R^{\bullet} + P$	$RO_2^{\bullet} + RO_2^{\bullet}$	$RO_2^{\bullet} + RO_2^{\bullet}$	$RO_2^{\bullet} + R^{\bullet}$	$R^{\bullet} + RO_2^{\bullet}$
$\mathbf{R_{prim,end}}$	$1.0\ 10^{-14}$	0.0	$1.0\ 10^{-22}$	0.0	$8.0\ 10^{-9}$	$3.0\ 10^{-19}$	$1.0\ 10^{-19}$
$\mathbf{R_{tert,end}}$	$7.0\ 10^{-13}$	$8.0\ 10^{-9}$	$5.0\ 10^{-17}$	$1.0\ 10^{-9}$	0.0	$3.0\ 10^{-20}$	$1.0\ 10^{-19}$
$\mathbf{R_{sec,mid}}$	$2.0\ 10^{-17}$	0.0	$3.0\ 10^{-19}$	0.0	$8.0\ 10^{-9}$	$1.0\ 10^{-23}$	$1.0\ 10^{-19}$

Table S12. Summary of *k*MC model output related to reaction rates (mol L^{-1} s^{-1}) of competitive reactions for poly(isobutylene) with a higher initiation rate coefficient ($k_{ini} = 100k_{ini}$); reaction rates as a function of time are given in Figure S26 to S28; red: lowest reaction rates; green: largest reaction rates; values indicated in black are set equal to 0.

1st reaction partner	***Propagation***				***Termination***		
	$RO_2^{\bullet} + P$	$RO^{\bullet} + P$	$R^{\bullet} + P$	$RO_2^{\bullet} + RO_2^{\bullet}$	$RO_2^{\bullet} + RO_2^{\bullet}$	$RO_2^{\bullet} + R^{\bullet}$	$R^{\bullet} + RO_2^{\bullet}$
$\mathbf{R_{prim,end}}$	$3.0\ 10^{-14}$	0.0	$2.0\ 10^{-18}$	0.0	$8.0\ 10^{-8}$	$7.0\ 10^{-15}$	$3.0\ 10^{-15}$
$\mathbf{R_{tert,end}}$	$7.0\ 10^{-12}$	$8.0\ 10^{-8}$	$5.0\ 10^{-13}$	$4.0\ 10^{-8}$	0.0	$3.0\ 10^{-15}$	$3.0\ 10^{-15}$
$\mathbf{R_{sec,mid}}$	$1.0\ 10^{-15}$	0.0	$3.0\ 10^{-15}$	0.0	$8.0\ 10^{-8}$	$5.0\ 10^{-18}$	$3.0\ 10^{-15}$

S5. References

1. Maillard, B.; Ingold, K. U.; Scaiano, J. C. *Journal of the American Chemical Society* **1983,** 105 (15), 5095-5099.
2. Gryn'ova, G.; Hodgson, J. L.; Coote, M. L. *Org. Biomol. Chem.* **2011,** 9 (2), 480-490.
3. Sabbe, M. K.; Reyniers, M.-F.; Van Speybroeck, V.; Waroquier, M.; Marin, G. B. *ChemPhysChem* **2008,** 9 (1), 124-140.
4. Denisov, E. T.; Denisova, T. G., *Handbook of Antioxidants. Bond Dissociation Energies, Rate Constants, Activation Energies and Enthalpies of Reaction, 2th Editions*. CRC Press: Boca Raton: Moscow, Russia, 1999.
5. Brandup, J.; Immergut, E. H.; Grulke, E. A., *Polymer Handbook, 4th Edition*. John Wiley & Sons: 1999.
6. Roland, C. M.; Boehm, G. G. A. *Macromolecules* **1985,** 18 (6), 1310-1314.
7. Lee, R.; Gryn'ova, G.; Ingold, K. U.; Coote, M. L. *Phys. Chem. Chem. Phys.* **2016,** 18 (34), 23673-23679.
8. Ingold, K. U., Group 2: Molecules and Radicals - Radical Reaction Rates in Liquids. Fischer, H., Ed. Springer-Verlag: Berlin, 1994; Vol. 18.
9. Neta, P.; Huie, R. E.; Ross, A. B. *Journal of Physical and Chemical Reference Data* **1990,** 19 (2), 413-513.