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# New Insight into the Formation of Structural Defects in Poly(vinyl chloride)

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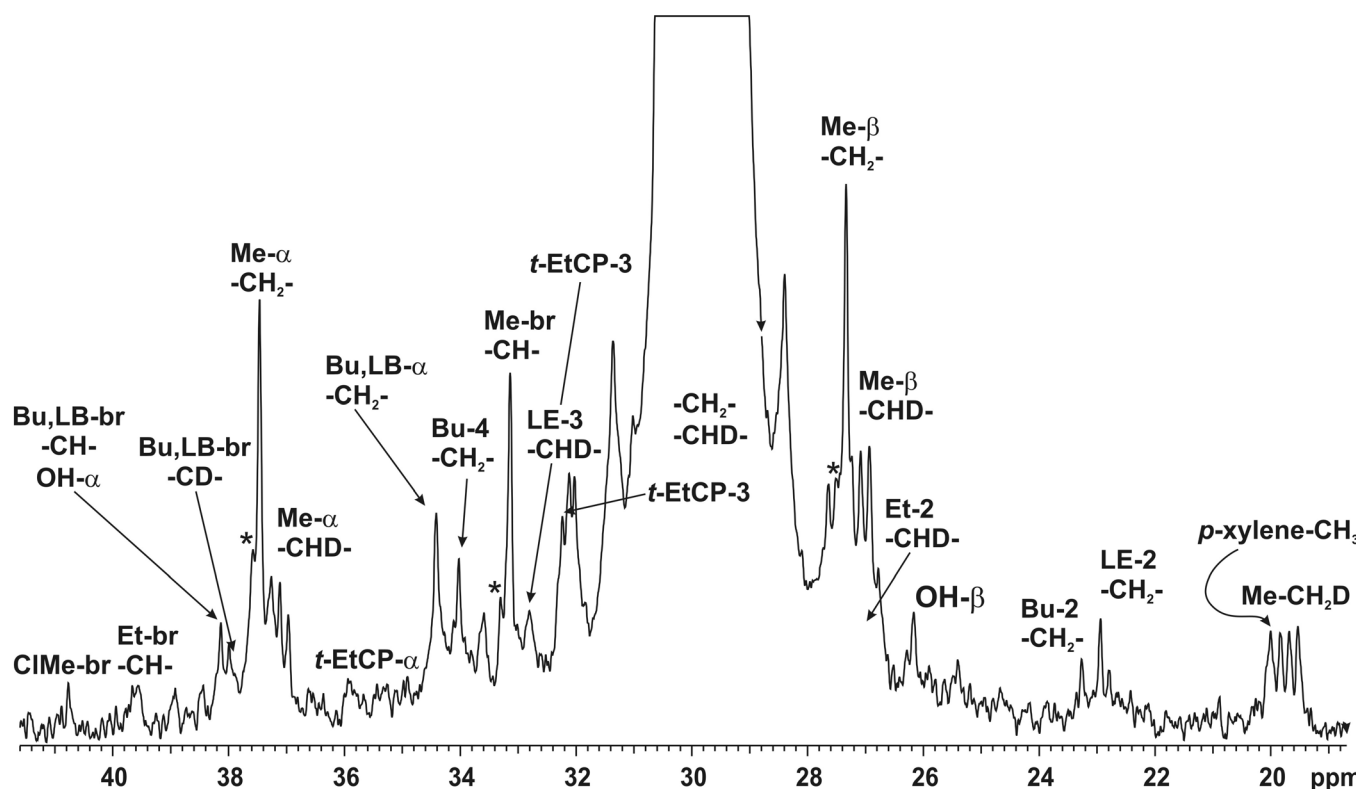
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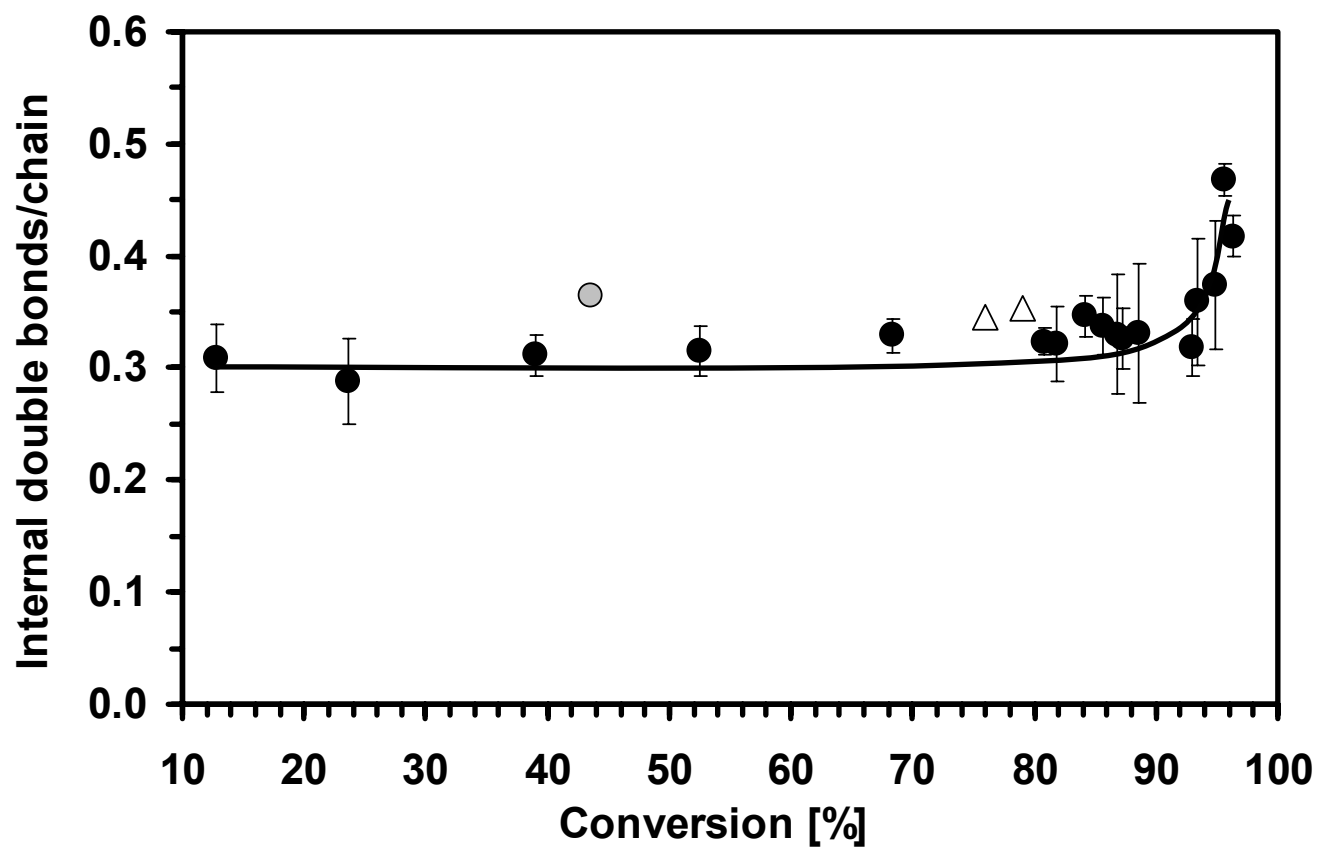
## **SUPPORTING INFORMATION**

(Figures S1–S4 and Tables S1–S3: 11 pages total)

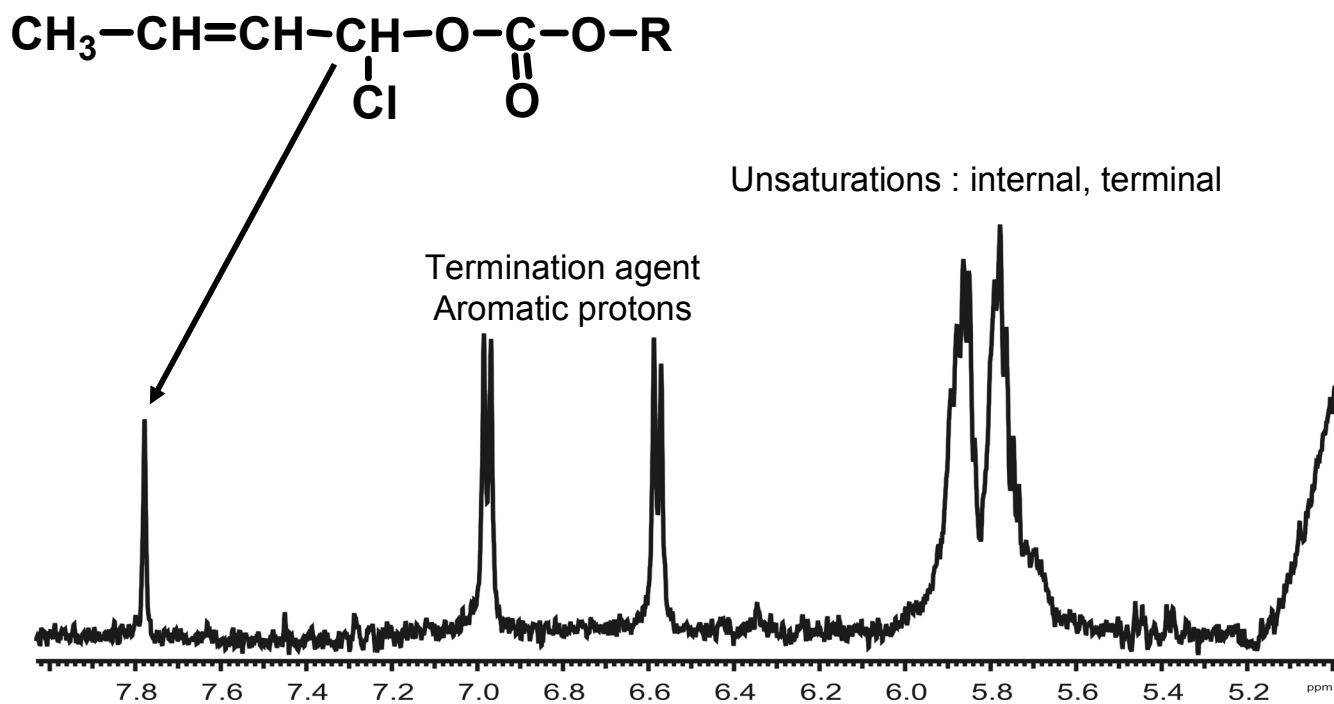
**Figure S1.**  $^{13}\text{C}$ -NMR spectrum of PVC reduced with (B)  $\text{Bu}_3\text{SnD}$ . Me = methyl, ClMe = chloromethyl, Et = ethyl, Bu = butyl, LB=long branch; LE = long chain end. Br = branch point carbon;  $\alpha, \beta$  = positions of the carbons in the main chain with respect to the branch point carbon, 1-4 = positions of the carbons in the corresponding branch with respect to the branch point carbon, where lower the number more remote the carbon. Peaks marked with \* are products of reduction with  $\text{Bu}_3\text{SnH}$ , contained in  $\text{Bu}_3\text{SnD}$ .



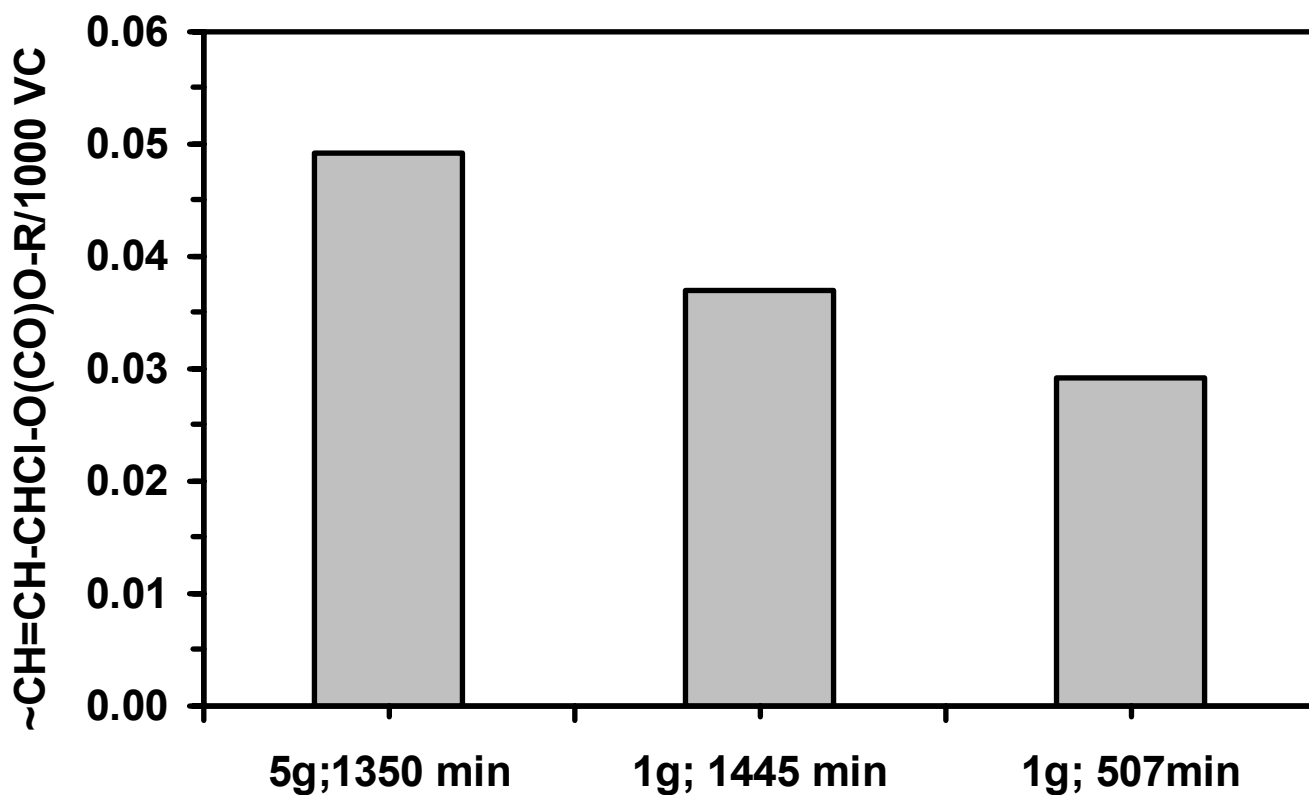
**Figure S2.** Dependence of the number of internal double bonds per chain on monomer conversion and amount of crotyl chloride present in the reaction mixture. —●— 0g;  $\triangle$  1g;  $\circ$  5g of crotylchloride added.



**Figure S3.** Expansion of a  $^1\text{H}$ -NMR spectrum of PVC sample synthesized in presence of 5g of crotyl chloride.



**Figure S4.** Correlation of the number of the amount of crotyl chloride present during the polymerization, reaction time and the number of end groups formed by combination of crotyl chloride allylic radicals with primary radicals.



**Table S1.** Summary of  $^{13}\text{C}$  chemical shifts of an 87.2% conversion sample reduced with  $\text{Bu}_3\text{SnH}$  and  $\text{Bu}_3\text{SnD}$ .

CARBON	Reduction with $\text{Bu}_3\text{SnH}$	CARBON	Reduction with $\text{Bu}_3\text{SnD}$	Isotope shift
— $\text{CH}_2$ —	30.00	— $\text{CH}_2$ —	29.88	0.12
		— $\text{CHD}$ —	29.60	0.40
Me – br	33.23	— $\text{CH}$ —	33.11	0.12
Me – $\alpha$	37.53	— $\text{CH}_2$ —	37.45	0.08
		— $\text{CHD}$ —	37.11	0.42
Me – $\beta$	27.44	— $\text{CH}_2$ —	27.32	0.12
		— $\text{CHD}$ —	27.04	0.40
Me – $\text{CH}_3$	19.92	— $\text{CH}_2\text{D}$ —	19.69	0.23
ClMe – br	40.77			
ClMe – $\text{CH}_2\text{Cl}$	48.81			
Et – br	39.67	— $\text{CH}$ —	39.62	0.05
Et – $\alpha$	34.02		Not detectable	
Et – $\beta$	27.28		Not detectable	
Et – 2	26.80	— $\text{CH}_2\text{D}$ —	26.61	0.19
Et – $\text{CH}_3$	11.64 (weak)			
Bu, LB – br	38.15	— $\text{CH}$ —	38.13	0.02
		— $\text{CD}$ —	37.75	0.40
Bu, LB – $\alpha$	34.52	— $\text{CH}_2$ —	34.40	0.12
		— $\text{CHD}$ —	34.26	0.26
Bu, LB – $\beta$	27.28	— $\text{CH}_2$ —	27.09	0.19
		— $\text{CHD}$ —	26.93	0.35
Bu – 2	23.38		Not detectable	
Bu – 3	29.57		Not detectable	
Bu – 4	34.12	— $\text{CH}_2$ —	34.01	0.11
Bu – $\text{CH}_3$	14.09	— $\text{CH}_2\text{D}$ —	13.72	0.37
		— $\text{CHD}$ —	26.93	0.35
ClBu – $\text{CH}_2\text{Cl}$	44.54			
LE, LB – $\text{CH}_3$	14.02	— $\text{CH}_2\text{D}$ —	13.72	0.30
LE – 2	22.85		Not detectable	
LE – 3	32.20		Not detectable	
Me-LB- $\alpha$	32.70		Not detectable	
Me-LB- $\alpha$	35.40		Not detectable	
Me-LB-br	40.10		Not detectable	
OH-br	71.87		71.87	0
OH- $\alpha$	38.23 (overlapped)		38.23	0
OH- $\beta$	26.02		26.02	0
<i>t</i> -EtCP- $\alpha$	35.85	— $\text{CH}_2$ —	35.90	-0.05
<i>t</i> -EtCP-3	32.84	— $\text{CH}_2$ —	32.82	0.02
<i>t</i> -EtCP-4	24.30		Not detectable	
<i>t</i> -EtCP-5	32.38		32.24	0.14

**Table S2.** GAUSSIAN Archive Entries for the Optimized Geometries

**Intramolecular 1–2 Hydrogen Shift TS (1)**

```
1\1\GINC-LC134\FTS\UmPWPW91\6-31+G(d,p)\C4H7Cl2(2)\MLC501\16-Apr-2004\
0\#\ MPWPW91/6-31+G** OPT=(TS,CALCFC,NOEIGENTEST,MAXCYC=300) IOP(3/76=
0572004280) MAXDISK=268435456\TS_12-cla-mpw1k\0,2\H,-2.2984250361,-1
.4454705551,0.1854591464\C,-1.5277916042,-0.8678849298,-0.2984610713\C
,-0.12026048,-1.1801083183,-0.0004882992\C,0.9876583479,-0.2281745236,
-0.1958761265\H,0.0261566878,-1.9957204702,0.6945731714\Cl,1.094473310
5,0.8673844269,1.2728959442\H,0.7698119505,0.4593391723,-1.0073094815\
C,2.3297098779,-0.8921757807,-0.3934800075\H,3.119143267,-0.1503255257
,-0.4699431628\H,2.3129969432,-1.4810048457,-1.3092353922\H,2.56090063
78,-1.5529918454,0.4387665517\H,-0.7610996067,-1.5717317128,-1.0661748
029\Cl,-2.0206722336,0.7060254024,-0.8103255327\Version=x86-Linux-G03
RevB.03\State=2-A\HF=-1076.9094942\S2=0.764295\S2-1=0.\S2A=0.750088\RM
SD=7.206e-09\RMSF=4.070e-06\Dipole=0.1261422,-1.1462636,-0.5335279\PG=
C01 [X(C4H7Cl2)]\@\
```

**Intermolecular 1–2 Hydrogen Shift TS (2)**

```
1\1\GINC-LC29\FTS\UmPWPW91\6-31+G(d,p)\C8H15Cl4(2)\MLC501\23-Apr-2004\
0\#\ MPWPW91/6-31+G** OPT=(TS,CALCFC,NOEIGENTEST,MAXCYC=300) IOP(3/76=
0572004280) MAXDISK=402653184 GEOM=CHECK\TS_inter-clb-mpw1k\0,2\C,2.
0219012844,2.1659713826,1.0389752203\C,2.0299334392,0.6721778478,0.819
8715294\C,1.4980298204,0.2563704084,-0.5207642468\C,1.5732880129,-1.18
99820283,-0.8779994037\Cl,3.2773638481,-1.7176846323,-1.1248524594\H,1
.1726439703,-1.8260021193,-0.0960856804\H,1.0583957098,-1.3964914809,-
1.809748361\H,3.0388535107,0.2796046974,0.9408888468\Cl,1.0979309493,-
0.1349012635,2.146817287\H,2.4264237663,2.4137731901,2.0159115827\H,2.
6402369719,2.6427082151,0.2797670534\H,1.0171138319,2.5723905147,0.962
2805006\H,1.8903382993,0.8988942019,-1.3066292558\H,0.1851946971,0.578
5812504,-0.6110019759\C,-1.0711503636,0.9559883892,-0.9142157116\C,-1.
9942523548,0.6807718441,0.2353011328\C,-2.1445877194,-0.7918580704,0.5
651568321\C,-3.0178879667,-1.017966432,1.7757571992\H,-3.1267903211,-2
.0784016348,1.9835366595\H,-2.5620332491,-0.542565901,2.643062417\H,-4
.0077762088,-0.5925222769,1.625813572\H,-1.1692981835,-1.2416664,0.722
720506\Cl,-2.8404166595,-1.6757677811,-0.8459703321\H,-1.6228583448,1.
1837750914,1.128663827\H,-2.979059745,1.0998523663,0.0161933853\H,-1.2
859644679,0.3917718147,-1.814716755\Cl,-0.9494113821,2.6593806429,-1.3
179445915\Version=x86-Linux-G03RevB.03\State=2-A\HF=-2154.606477\S2=0
.76312\S2-1=0.\S2A=0.750086\RMSD=9.872e-09\RMSF=1.992e-06\Dipole=-0.18
99162,0.5414363,0.4412622\PG=C01 [X(C8H15Cl4)]\@\
```

**Propagation TS (3)**

```
1\1\GINC-LC57\FTS\UmPWPW91\6-31+G(d,p)\C6H10Cl3(2)\MLC501\19-Apr-2004\
0\#\ MPWPW91/6-31+G** OPT=(TS,CALCFC,NOEIGENTEST,MAXCYC=300) IOP(3/76=
0572004280) MAXDISK=268435456\TS_prop-clb-mpw1k\0,2\C,-1.7437352777,
0.2719167108,-2.5825861584\C,-1.7263494206,0.2994559595,-1.0730537943\
C,-0.3118589554,0.2559637659,-0.5090516526\C,-0.2184696194,0.363939004
7,0.9698580747\C,2.024163103,0.1798915736,1.4568913674\C,2.5441607861,
-0.9499635219,0.9403321013\Cl,3.1953140587,-1.0286218619,-0.6523208151
\H,2.15426672298,-1.9000148759,1.448332945\H,2.1666313,1.1325070227,0.9
705465902\H,1.7591630238,0.1919093124,2.5028487929\H,-0.566202558,-0.4
600014393,1.57370051\Cl,-0.6522197582,1.8939425375,1.6590116266\H,0.16
35098198,-0.6761490061,-0.8140736418\H,0.2479366674,1.0717035217,-0.97
03353015\Cl,-2.6750808519,-1.0935256487,-0.4381146336\H,-2.2439556826,
1.1797761247,-0.7016733784\H,-2.7622653841,0.2898884705,-2.95984802\H,
-1.2523720647,-0.6219687622,-2.9604307547\H,-1.2188046742,1.1446132174
,-2.9692023938\Version=x86-Linux-G03RevB.03\State=2-A\HF=-1615.153108
4\S2=0.811018\S2-1=0.\S2A=0.750661\RMSD=3.733e-09\RMSF=2.872e-06\Dipol
e=0.247431,0.1867976,-0.1426937\PG=C01 [X(C6H10Cl3)]\@\
```



### CH<sub>3</sub>CHCICH<sub>2</sub>CHCl (4)

```
1\1\GINC-SC33\FOpt\UmPWPW91\6-31+G(d,p)\C4H7Cl2(2)\MLC501\14-Apr-2004\1\
1\#\ MPWPW91/6-31+G** OPT=(Z-MATRIX) IOP(3/76=0572004280) MAXDISK=4026
53184\VC_dim-alb3-mpw1k\0,2\Cl\C,1,B1\C,2,B2,1,A1\C,3,B3,2,A2,1,D1,0
\C,4,B4,3,A3,2,D2,0\H,5,B5,4,A4,3,D3,0\H,5,B6,4,A5,6,D4,0\H,5,B7,4,A6,
6,D5,0\H,4,B8,3,A7,5,D6,0\Cl,4,B9,3,A8,5,D7,0\H,3,B10,2,A9,4,D8,0\H,3,
B11,2,A10,4,D9,0\H,2,B12,1,A11,3,D10,0\B1=1.7100974\B2=1.47913401\B3=
1.52582632\B4=1.50967334\B5=1.08938868\B6=1.08795147\B7=1.08622144\B8=
1.08677858\B9=1.79909171\B10=1.09013363\B11=1.092319\B12=1.07623822\A1
=118.93143509\A2=115.11045059\A3=112.49193855\A4=109.59177335\A5=110.9
3481628\A6=110.95981522\A7=109.5503404\A8=109.50743974\A9=108.62620972
\A10=109.45666991\A11=114.80030059\D1=-72.22678588\D2=175.65997687\D3=
-61.0951825\D4=119.83866499\D5=-119.64255703\D6=-123.41887671\D7=122.0
7417007\D8=-122.27946377\D9=120.64198249\D10=198.4315163\Version=DEC-
AXP-OSF/1-G03RevB.03\State=2-A\HF=-1076.9843764\S2=0.756222\S2-1=0.\S2
A=0.750028\RMSD=5.099e-09\RMSF=1.580e-05\Dipole=0.6154789,0.5170614,0.
2482111\PG=C01 [X(C4H7Cl2)]\ \@
```

### CH<sub>3</sub>CHCICH<sub>2</sub>CH<sub>2</sub>Cl (5)

```
1\1\GINC-SC75\FOpt\RmPWPW91\6-31+G(d,p)\C4H8Cl2\MLC501\14-Apr-2004\1\
#\ MPWPW91/6-31+G** OPT=(Z-MATRIX) IOP(3/76=0572004280) MAXDISK=4026531
84\VC_dim-alb3-mpw1k\0,1\Cl\C,1,B1\C,2,B2,1,A1\C,3,B3,2,A2,1,D1,0\C
,4,B4,3,A3,2,D2,0\H,5,B5,4,A4,3,D3,0\H,5,B6,4,A5,6,D4,0\H,5,B7,4,A6,6,
D5,0\H,4,B8,3,A7,5,D6,0\Cl,4,B9,3,A8,5,D7,0\H,3,B10,2,A9,4,D8,0\H,3,B1
1,2,A10,4,D9,0\H,2,B12,1,A11,3,D10,0\H,2,B13,1,A12,3,D11,0\B1=1.78686
902\B2=1.50997784\B3=1.51522035\B4=1.5100198\B5=1.08934449\B6=1.088030
06\B7=1.08611653\B8=1.08647547\B9=1.80251049\B10=1.09135557\B11=1.0907
548\B12=1.08450879\B13=1.0847467\A1=111.94166562\A2=115.39664593\A3=11
2.5303665\A4=109.47292176\A5=111.01243922\A6=111.01740317\A7=109.89971
001\A8=109.6739706\A9=107.92583435\A10=109.15685931\A11=106.44095338\A
12=106.8177579\D1=-65.01349317\D2=174.89725479\D3=-61.4098539\D4=119.7
8707264\D5=-119.58186037\D6=-123.52868403\D7=121.85691469\D8=-122.1781
4818\D9=121.6072868\D10=121.09062733\D11=-122.35969678\Version=DEC-AX
P-OSF/1-G03RevB.03\State=1-A\HF=-1077.6500395\RMSD=4.765e-09\RMSF=6.24
0e-05\Dipole=0.4802076,0.7098528,0.5058297\PG=C01 [X(C4H8Cl2)]\ \@
```

### CH<sub>3</sub>CHCICH·CH<sub>2</sub>Cl (6)

```
1\1\GINC-SC80\FOpt\UmPWPW91\6-31+G(d,p)\C4H7Cl2(2)\MLC501\15-Apr-2004\
0\#\ MPWPW91/6-31+G** OPT=(Z-MATRIX) IOP(3/76=0572004280) MAXDISK=2684
35456 GEOM=CHECK GUESS=READ\VC_shift-alb3-mpw1k\0,2\Cl,-2.5810514627
,0.1185769071,-0.3784543444\C,-1.2914711025,-0.7372521258,0.5747278425
\C,-0.1590760413,0.1562049803,0.8470416467\C,0.8538485599,0.4402850243
,-0.1823457444\C,1.6010688994,1.733539499,0.0289844781\H,0.8967066766,
2.5636617308,-0.0023559746\H,2.1005509826,1.7372681031,0.9952003461\H,
2.3481254634,1.8823552771,-0.7451643693\H,0.4092064078,0.4047438251,-1
.1737893558\Cl,2.0545399648,-0.9465950054,-0.2070930154\H,-0.052198466
9,0.6038263981,1.8244109074\H,-1.7742826045,-1.0833607771,1.4804052149
\H,-1.0036348877,-1.5888511534,-0.0348509886\Version=DEC-AXP-OSF/1-G0
3RevB.03\State=2-A\HF=-1076.9844005\S2=0.757916\S2-1=0.\S2A=0.75005\RM
SD=3.151e-09\RMSF=9.038e-05\Dipole=0.0965802,0.374588,0.4769056\PG=C01
[X(C4H7Cl2)]\ \@
```

### CH<sub>2</sub>=CHCl (7)

```
1\1\GINC-SC122\FOpt\RmPWPW91\6-31+G(d,p)\C2H3Cl1\MLC501\15-Apr-2004\0\
#\ MPWPW91/6-31+G** OPT IOP(3/76=0572004280) MAXDISK=134217728\VC_mon
-cs-mpw1k\0,1\H,-0.784717183,0.,-2.4937928559\C,-0.8487498073,0.,-1.4
166758073\C,0.2623435314,0.,-0.7048755763\H,-1.8258894399,0.,-0.960003
9454\H,1.249714969,0.,-1.1377794688\Cl,0.2870193711,0.,1.018875563\Ve
rsion=DEC-AXP-OSF/1-G03RevB.03\State=1-A\HF=-538.1761332\RMSD=2.411e-
09\RMSF=2.466e-05\Dipole=-0.0510812,0.,-0.6300194\PG=CS [SG(C2H3Cl1)]\
\ \@
```

**CH<sub>2</sub>Cl-CH=CH-CH<sub>2</sub>-CH<sub>2</sub>Cl (8)**

1\1\GINC-SC2\FOpt\RmPWPW91\6-31+G(d,p)\C5H8Cl2\MLC501\04-Oct-2004\0\#\#  
MPWPW91/6-31+G\*\* IOP(3/76=0572004280) OPT GEOM=CHECK GUESS=READ MAXDI  
SK=134217728\macmon-alb1c3d3-mpw1k\0,1\C,2.5969719468,0.7460286736,0  
.1331271412\C,1.2201343563,0.6624005355,-0.4115501468\C,0.1297744036,0  
.843386333,0.3240010987\C,-1.267024055,0.7861566866,-0.2008305663\H,1.  
1329299804,0.4513629873,-1.4704536436\H,0.2408051682,1.0415874366,1.38  
54431801\Cl,3.4626204578,-0.8167069273,-0.037373003\H,3.1984821122,1.4  
732438312,-0.4036315778\H,2.5962189916,0.994357514,1.1890426782\C,-2.0  
264834822,-0.365458724,0.4284674775\H,-1.7896456653,1.7164895354,0.024  
9300654\H,-1.2627667762,0.6719417897,-1.2831756035\H,-2.0528546989,-0.  
2810705313,1.5106679363\H,-1.5829616705,-1.3194560609,0.1631029957\Cl,  
-3.7214702495,-0.405854104,-0.1246985298\Version=DEC-AXP-OSF/1-G03Rev  
B.03\State=1-A\HF=-1115.7145837\RMSD=1.796e-09\RMSF=2.975e-06\Dipole=0  
.2883782,0.7889581,0.2936517\PG=C01 [X(C5H8Cl2)]\#@

**TS: CH<sub>3</sub>-CHCl-CH<sub>2</sub>-CHCl + CH<sub>2</sub>Cl-CH=CH-CH<sub>2</sub>-CH<sub>2</sub>Cl (9)**

1\1\GINC-SC77\FTS\UmPWPW91\6-31+G(d,p)\C9H15Cl4(2)\MLC501\06-Oct-2004\  
0\#\# MPWPW91/6-31+G\*\* OPT=(TS,CALCF,NOEIGENTEST,MAXCYC=300) IOP(3/76=  
0572004280) MAXDISK=402653184\Tsmacmon\_new-a2-mpw1k\0,2\C,-0.4277950  
589,-0.3186541535,-1.2580114832\C,0.9271953364,-0.1953668656,-1.240239  
3194\C,1.6485543204,1.106592854,-1.3192567135\C,-1.084027735,-1.648503  
873,-1.4024410143\H,-1.0283307206,0.53588624,-1.5440286208\H,1.5310080  
09,-1.0887221186,-1.1220862941\H,0.941444979,1.9346264244,-1.333915118  
9\H,2.2890492677,1.2441735706,-0.4458528522\C,2.5122439613,1.163462033  
3,-2.5660241373\H,1.9071748746,1.1138506706,-3.465103301\Cl,3.44156140  
44,2.6839398148,-2.6436037056\H,3.2347694311,0.3534729223,-2.585298836  
5\Cl,-1.3583225553,-2.0444631552,-3.1326502708\H,-0.4653756271,-2.4444  
192003,-1.0009844667\H,-2.0632627904,-1.675987307,-0.9387882001\C,-1.0  
872732991,0.1385509738,0.8760399575\C,-0.5637368479,-0.9494525373,1.74  
55786526\Cl,-2.8143595179,0.3121658867,0.8390442703\H,-0.6005168209,1.  
1006196537,0.9262422904\C,-0.7171165901,-0.7126360741,3.2432077216\H,-  
1.0761996744,-1.8852178651,1.5144991452\H,0.4944110868,-1.0864704833,1.  
.5187756524\C,-0.2604628623,-1.8970760547,4.0610582211\H,-1.7505456176  
, -0.467471582,3.4729432594\Cl,0.2223710827,0.744940586,3.7236313826\H,  
-0.3671739597,-1.6990430698,5.1236899131\H,-0.8658967079,-2.7678531565  
,3.8121660384\H,0.7826998861,-2.1308557642,3.8591015831\Version=DEC-A  
XP-OSF/1-G03RevB.03\State=2-A\HF=-2192.6867561\S2=0.819305\S2=1=0.\S2A  
=0.750753\RMSD=4.523e-09\RMSF=2.117e-06\Dipole=-0.051872,-1.185568,0.8  
424049\PG=C01 [X(C9H15Cl4)]\#@

**CH<sub>2</sub>Cl-CH=CH-CH<sub>3</sub> (for use in ONIOM-calculations of 8)**

1\1\GINC-SC11\FOpt\RmPWPW91\6-31+G(d,p)\C4H7Cl1\MLC501\07-Oct-2004\0\#\#  
MPWPW91/6-31+G\*\* IOP(3/76=0572004280) OPT MAXDISK=134217728\macmon\_  
small-mpw1k\0,1\C,-1.0093362801,-0.100107734,0.4991595776\C,0.4726383  
311,-0.1076528527,0.5114965917\C,1.2088621076,0.9973265102,0.488709834  
4\C,2.6964964124,1.0343528855,0.5233495138\H,0.9502526017,-1.079316666  
1,0.5460152072\H,0.7032359027,1.9561777594,0.4395614679\Cl,-1.66470611  
29,-0.8963619587,-0.9740895839\H,-1.4250260024,-0.6552820172,1.3344267  
672\H,-1.4047804044,0.9099643426,0.5109493057\H,3.0906186728,1.5319054  
445,-0.3629054378\H,3.0532285836,1.5968887695,1.3860715163\H,3.1205111  
387,0.0343028116,0.5691109939\Version=DEC-AXP-OSF/1-G03RevB.03\State=  
1-A\HF=-616.8027842\RMSD=8.663e-09\RMSF=3.339e-05\Dipole=0.5785138,0.5  
045518,0.6912087\PG=C01 [X(C4H7Cl1)]\#@

**TS: CH<sub>3</sub>-CHCl-CH<sub>2</sub>-CHCl + CH<sub>2</sub>Cl-CH=CH-CH<sub>3</sub> (for use in ONIOM-calculations of 9)**

1\1\GINC-SC74\FTS\UmPWPW91\6-31+G(d,p)\C8H14Cl3(2)\MLC501\08-Oct-2004\  
0\#\# MPWPW91/6-31+G\*\* OPT=(TS,CALCF,NOEIGENTEST,MAXCYC=300) IOP(3/76=  
0572004280) MAXDISK=402653184\Tsmacmon\_small-mpw1k\0,2\C,0.228893216  
1,0.257616477,-1.8189399931\C,1.5897743961,0.2598973693,-1.8158180355\  
C,2.4240965726,1.488961611,-1.781593982\C,-0.5457301238,-0.9927745753,  
-2.0517579972\H,-0.295939176,1.1810233115,-2.0300063113\H,2.1090133211

, -0.6912000534, -1.7777127112\H, 1.8172003459, 2.3874650628, -1.8676550837  
\H, 2.9991787966, 1.5553190629, -0.8559187958\H, 3.1470813015, 1.4912530404  
, -2.5978782848\Cl, -0.8952619424, -1.2263416122, -3.7996784235\H, 0.007745  
5702, -1.8700039411, -1.7326887294\H, -1.5136494721, -0.973449874, -1.56410  
06185\C, -0.3542460975, 0.6139079272, 0.356119448\C, 0.0863634353, -0.57366  
47297, 1.1366287311\Cl, -2.0615545903, 0.9402428064, 0.3824440159\H, 0.2160  
027872, 1.524335763, 0.4608324004\C, -0.0110959262, -0.4302037896, 2.650192  
8972\H, -0.5150240428, -1.4407737683, 0.8568798313\H, 1.1217100616, -0.7910  
243782, 0.8708221738\C, 0.3459701532, -1.7070721482, 3.3730480038\H, -1.009  
9888548, -0.1032171424, 2.9259886294\Cl, 1.0768219724, 0.8935705127, 3.2035  
051076\H, 0.2862668739, -1.5743989404, 4.4495097091\H, -0.3489800524, -2.49  
53696507, 3.0858725847\H, 1.3551363096, -2.0269863594, 3.1221788736\\Versi  
on=DEC-AXP-OSF/1-G03RevB.03\State=2-A\HF=-1693.7750987\S2=0.81907\S2-1  
=0.\S2A=0.750745\RMSD=4.658e-09\RMSF=7.446e-07\Dipole=0.5748111, -0.513  
5035, 0.6256018\PG=C01 [X(C8H14Cl3)]\ \@

**Table S3. Component Energies and Entropies Used in Calculating the Entries in Table 1<sup>a</sup>**

Species <sup>b</sup>	1	2	3	4	5	6	7	8	9
$E_0$ (Hartrees)	-1075.81572	-2152.42853	-1613.54171	-1075.88883	-1076.55872	-1075.88725	-537.65613	-1114.49571 <sup>c</sup>	-2190.38107 <sup>c</sup>
ZPVE (kJ mol <sup>-1</sup> )	247.7	546.1	373.5	259.2	295.9	258.6	110.2	309.2	571.8
$\Delta\Delta H$ (kJ mol <sup>-1</sup> )	26.3	53.5	39.3	26.8	25.9	27.4	13.6	29.3	55.5
$H_{\text{tot}}$ (kJ mol <sup>-1</sup> )	-2824280.2	-5650601.5	-4235941.0	-2824460.2	-2826183.1	-2824456.0	-1411492.4	-2925770.0	-5750218.2
$S_{\text{elect}}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	5.8	5.8	5.8	5.8	0.0	5.8	0.0	0	5.8
$S_{\text{trans}}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	171.1	179.8	176.1	171.1	171.2	171.1	162.4	172.3	180.4
$S_{\text{rot}}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	120.8	140.4	134.1	121.2	121.2	121.7	96.0	126.8	144.9
$S_{\text{vibr}}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	86.3	277.2	182.3	90.4	83.7	98.8	10.8	112.0	297.6
$S_{\text{tot}}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	384.0	603.1	498.3	388.5	376.1	397.3	269.2	411.2	628.6

<sup>a</sup>Shown here are the total energies at 0 K of each species ( $E_0$ ), as calculated at the G3(MP2)-RAD//MPW1K/6-31+G(d,p) level of theory, together with the zero-point vibrational energy (ZPVE), the thermal correction to enthalpy at 330.65 K ( $\Delta\Delta H$ ), and the total enthalpy at 330.65 K. Also shown are the electronic ( $S_{\text{elect}}$ ), translational ( $S_{\text{trans}}$ ), external rotation ( $S_{\text{rot}}$ ) and vibrational ( $S_{\text{vibr}}$ ) contributions to the total entropy at 330.65 K ( $S_{\text{tot}}$ ). These were calculated using geometries and frequencies calculated at the MPW1K/6-31+G(d,p) level of theory, under the harmonic oscillator approximation. <sup>b</sup>See Figure 13. <sup>c</sup>These were calculated at an “approximate” G3(MP2)-RAD level of theory via an ONIOM-based approach. In each case, the energy for the full-system at the RMP2/6-311+G(3df,2p) level of theory was corrected to the G3(MP2)-RAD level using calculations at both levels on the smaller models, CH<sub>2</sub>Cl-CH=CH-CH<sub>3</sub> (for 8) and the TS of CH<sub>3</sub>-CHCl-CH<sub>2</sub>-CHCl• + CH<sub>2</sub>Cl-CH=CH-CH<sub>3</sub> (for 9).