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

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SUPPORTING INFORMATION

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

Figure S1. ^{13}C-NMR spectrum of PVC reduced with (B) Bu_3SnD. Me = methyl, ClMe = chloromethyl, Et = ethyl, Bu = butyl, LB=long branch; LE = long chain end. Br = branch point carbon; α,β = 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 Bu_3SnH, contained in Bu_3SnD.

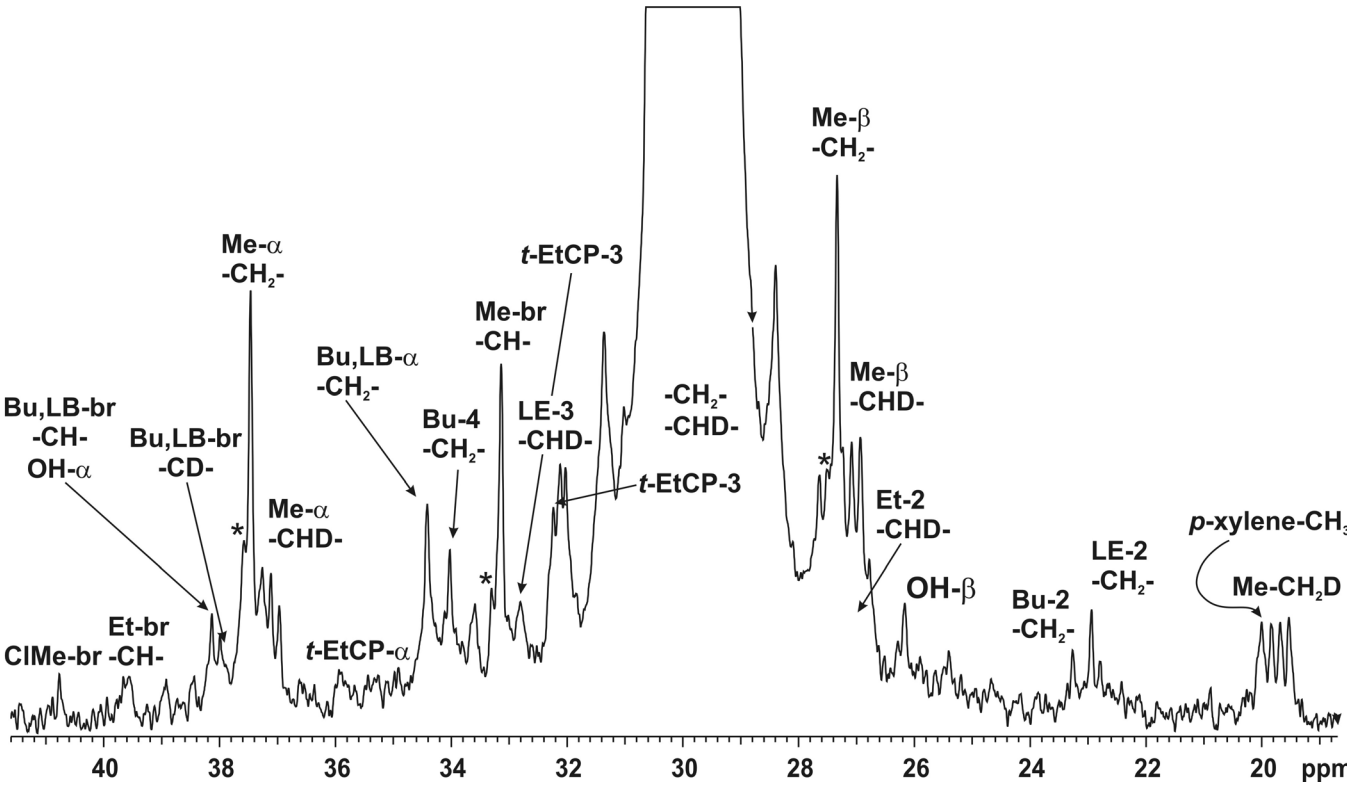

Figure S2. Dependence of the number of internal double bonds per chain on monomer conversion and amount of crotyl chloride present in the reaction mixture. —●— 0g; △1g; ◯ 5g of crotylchloride added.

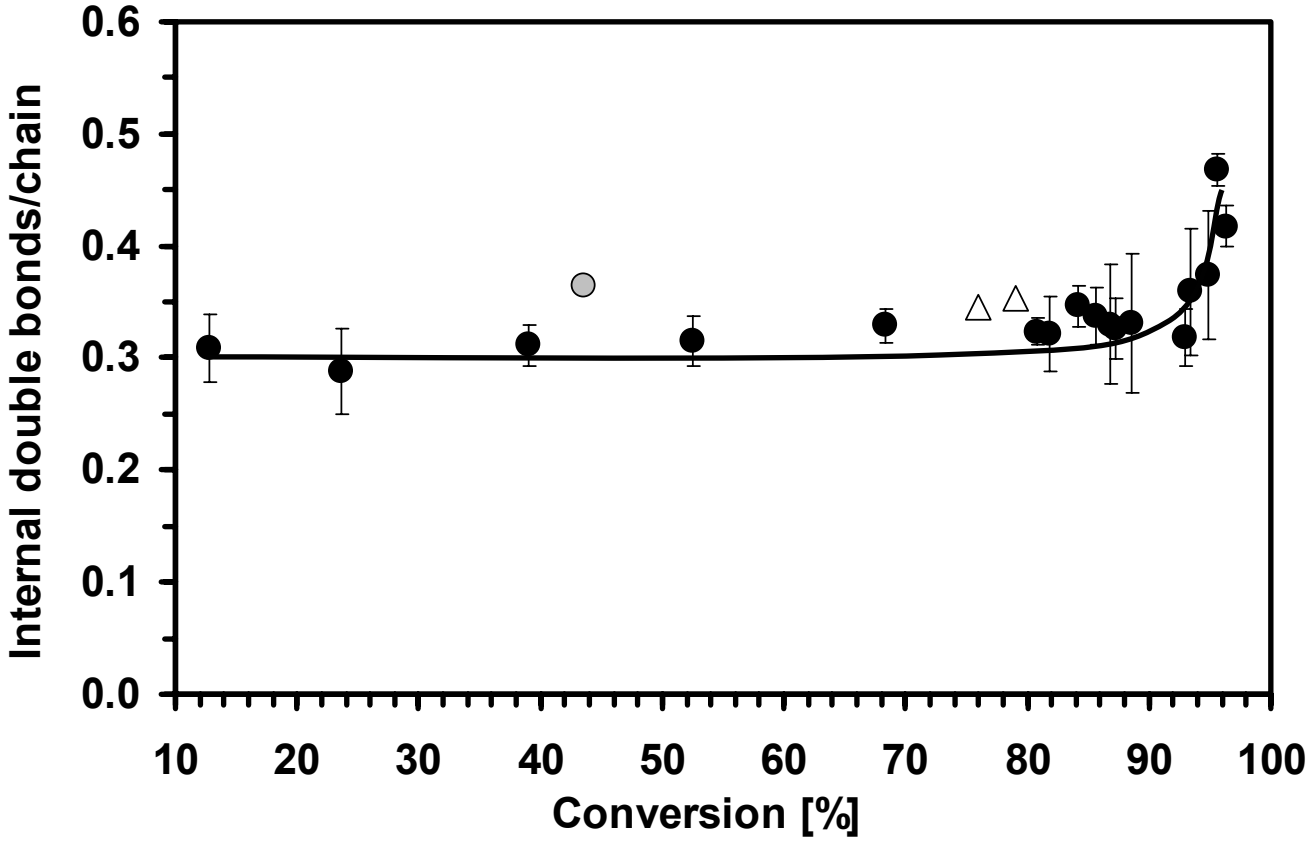

Figure S3. Expansion of a ^{1}H-NMR spectrum of PVC sample synthesized in presence of 5g of crotyl chloride.

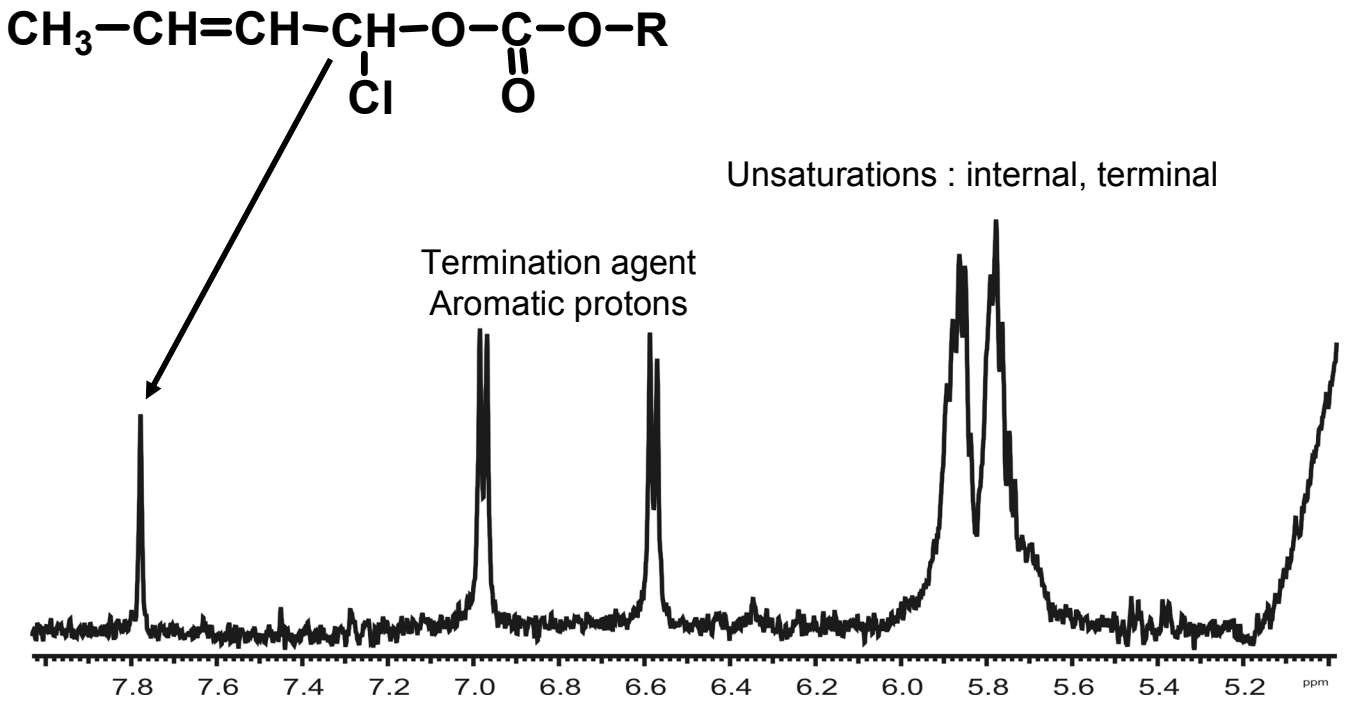

Figure S4. Correlation of the number of the amount of crotyl chloride present during the polymerization, reaction time and the number of end groups formed by combination of crotyl chloride allylic radicals with primary radicals.

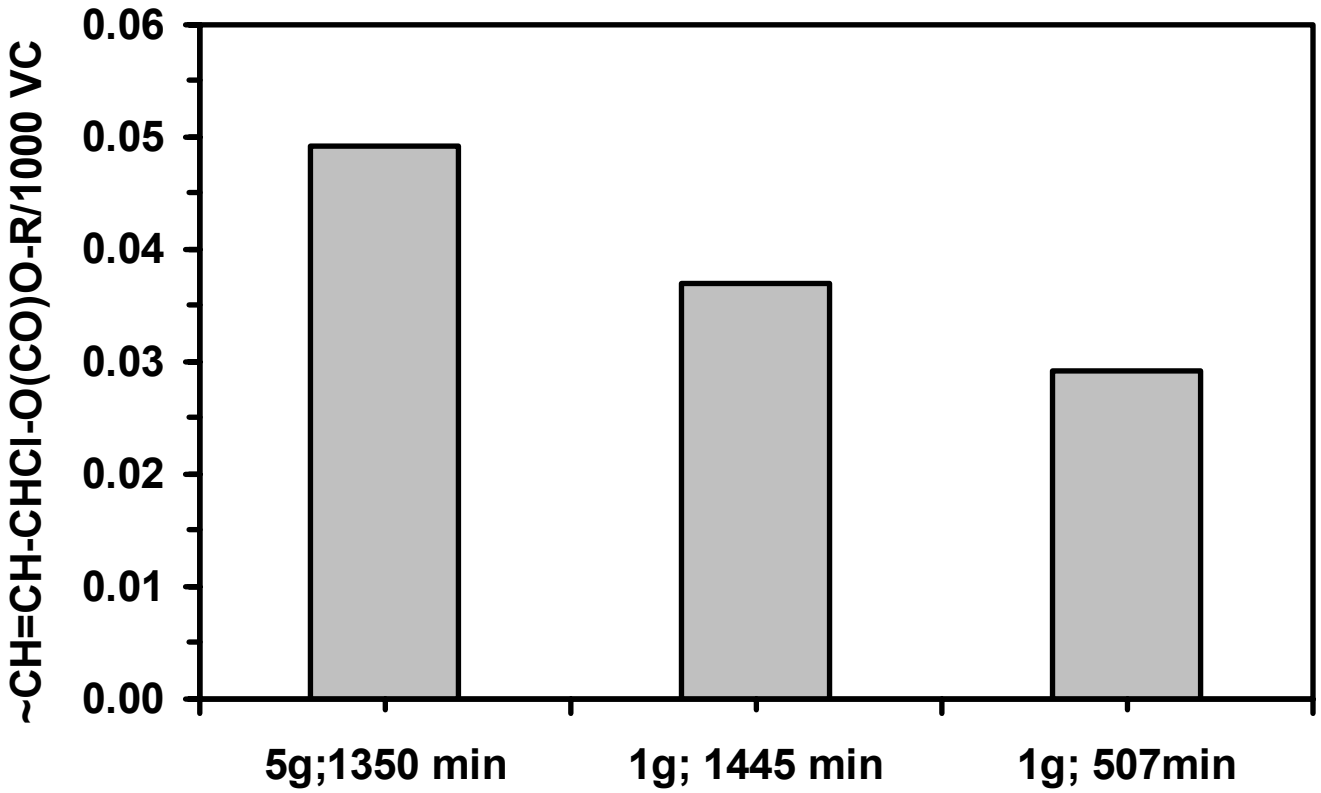

Table S1. Summary of ^{13}C chemical shifts of an 87.2% conversion sample reduced with Bu_3SnH and Bu_3SnD.

CARBON	Reduction with Bu_3SnH	CARBON	Reduction with Bu_3SnD	Isotope shift
— CH_2 —	30.00	— CH_2 —	29.88	0.12
		— CHD—	29.60	0.40
Me – br	33.23	— CH—	33.11	0.12
Me – α	37.53	— CH_2 —	37.45	0.08
		— CHD—	37.11	0.42
Me – β	27.44	— CH_2 —	27.32	0.12
		— CHD—	27.04	0.40
Me – CH_3	19.92	— CH_2D—	19.69	0.23
ClMe – br	40.77			
ClMe – CH_2Cl	48.81			
Et – br	39.67	— CH—	39.62	0.05
Et – α	34.02		Not detectable	
Et – β	27.28		Not detectable	
Et – 2	26.80	— CH_2D—	26.61	0.19
Et – CH_3	11.64 (weak)			
Bu, LB – br	38.15	— CH —	38.13	0.02
		— CD —	37.75	0.40
Bu, LB – α	34.52	— CH_2 —	34.40	0.12
		— CHD—	34.26	0.26
Bu, LB – β	27.28	— CH_2 —	27.09	0.19
		— CHD—	26.93	0.35
Bu – 2	23.38		Not detectable	
Bu – 3	29.57		Not detectable	
Bu – 4	34.12	— CH_2 —	34.01	0.11
Bu – CH_3	14.09	— CH_2D—	13.72	0.37
		— CHD—	26.93	0.35
ClBu – CH_2Cl	44.54			
LE, LB – CH_3	14.02	— CH_2D—	13.72	0.30
LE – 2	22.85		Not detectable	
LE – 3	32.20		Not detectable	
Me-LB-α	32.70		Not detectable	
Me-LB-α	35.40		Not detectable	
Me-LB-br	40.10		Not detectable	
OH-br	71.87		71.87	0
OH-α	38.23 (overlapped)		38.23	0
OH-β	26.02		26.02	0
t-EtCP-α	35.85	— CH_2 —	35.90	-0.05
t-EtCP-3	32.84	— CH_2 —	32.82	0.02
t-EtCP-4	24.30		Not detectable	
t-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-c1a-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-c1b-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
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```


Propagation TS (*3*)


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 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,2.5426672298,-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)]\\@
```

$CH_3CHClCH_2CHCl•$ (*4*)

```
1\1\GINC-SC33\FOpt\UmPWPW91\6-31+G(d,p)\C4H7Cl2(2)\MLC501\14-Apr-2004\
 1\\# MPWPW91/6-31+G** OPT=(Z-MATRIX) IOP(3/76=0572004280) MAXDISK=4026
 53184\\VC_dim-a1b3-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)]\\@
```

$CH_3CHClCH_2CH_2Cl$ (*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\\PVC_dim-a1b3-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)]\\@
```

$CH_3CHClCH•CH_2Cl$ (*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-a1b3-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)]\\@
```

$CH_2=CHCl$ (*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)]\
 \@
```

$CH_2Cl–CH=CH–CH_2–CH_2Cl$ (*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-a1b1c3d3-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: $CH_3–CHCl–CH_2–CHCl•$ + $CH_2Cl–CH=CH–CH_2–CH_2Cl$ (*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,CALCFC,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)]\\@
```


$CH_2Cl–CH=CH–CH_3$ (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: $CH_3–CHCl–CH_2–CHCl•$ + $CH_2Cl–CH=CH–CH_3$ (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,CALCFC,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[a]

Species[b]	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[c]	-2190.38107[c]
ZPVE (kJ mol^{-1})	247.7	546.1	373.5	259.2	295.9	258.6	110.2	309.2	571.8
$\Delta\Delta$H (kJ mol^{-1})	26.3	53.5	39.3	26.8	25.9	27.4	13.6	29.3	55.5
H_{tot} (kJ mol^{-1})	-2824280.2	-5650601.5	-4235941.0	-2824460.2	-2826183.1	-2824456.0	-1411492.4	-2925770.0	-5750218.2
S_{elect} (J mol^{-1} K^{-1})	5.8	5.8	5.8	5.8	0.0	5.8	0.0	0	5.8
S_{trans} (J mol^{-1} K^{-1})	171.1	179.8	176.1	171.1	171.2	171.1	162.4	172.3	180.4
S_{rot} (J mol^{-1} K^{-1})	120.8	140.4	134.1	121.2	121.2	121.7	96.0	126.8	144.9
S_{vibr} (J mol^{-1} K^{-1})	86.3	277.2	182.3	90.4	83.7	98.8	10.8	112.0	297.6
S_{tot} (J mol^{-1} K^{-1})	384.0	603.1	498.3	388.5	376.1	397.3	269.2	411.2	628.6

[a]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_{elect}), translational (S_{trans}), external rotation (S_{rot}) and vibrational (S_{vibr}) contributions to the total entropy at 330.65 K (S_{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. [b]See Figure 13. [c]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, $CH_2Cl–CH=CH–CH_3$ (for 8) and the TS of $CH_3–CHCl–CH_2–CHCl\bullet + CH_2Cl–CH=CH–CH_3$ (for 9).