University of Groningen

Experimental and theoretical evaluation of the reactions leading to formation of internal double bonds in suspension PVC

Purmová, Jindra; Pauwels, Kim F. D.; Agostini, Michela; Bruinsma, Maarten; Vorenkamp, Eltjo J.; Schouten, Arend J.; Coote, Michelle L.

Published in:
Macromolecules

DOI:
[10.1021/ma800583k](https://doi.org/10.1021/ma800583k)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2008

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Purmová, J., Pauwels, K. F. D., Agostini, M., Bruinsma, M., Vorenkamp, E. J., Schouten, A. J., & Coote, M. L. (2008). Experimental and theoretical evaluation of the reactions leading to formation of internal double bonds in suspension PVC. *Macromolecules*, 41(15), 5527-5539. <https://doi.org/10.1021/ma800583k>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Experimental and Theoretical Evidence for Backbiting as a Main Source of Internal Double Bonds in Suspension PVC

*Jindra Purmová¹, Kim F.D. Pauwels, Michela Agostini, Maarten Bruinsma, Joop E. Vorenkamp
and Arend J. Schouten**

Department of Polymer Science, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

¹ Present address, Dept CAP-CWA, Research & Technology Center, Akzo Nobel Chemicals, Velperweg 76, 6824 BM Arnhem, The Netherlands

Michelle L. Coote*

ARC Centre for Free-Radical Chemistry and Biotechnology, Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia

SUPPORTING INFORMATION

(**Table S1, S2, Figure S1; APPENDIX I:** Calculations of the numbers of defect structures from NMR spectra, **APPENDIX II:** Description of the diffusion controlled rate coefficients and calculation of polymer fraction in polymer-rich phase, **APPENDIX III:** Description of the calculation of ratios of the reaction rates, probabilities of side reactions and molar concentrations of polymer and monomer in the polymer rich phase: 28 pages total)

Table S1. Characteristics of the PVC samples of different monomer conversions and their fractions and low molecular weight extracts.

Conversion [%]	Original PVC			Fractionated PVC		
	$\overline{Mn}$ [kg mol ⁻¹]	$\overline{Mw}$ [kg mol ⁻¹]	$\overline{D}$	$\overline{Mn}$ [kg mol ⁻¹]	$\overline{Mw}$ [kg mol ⁻¹]	$\overline{D}$
23.7	42.60	80.95	1.90	87.60	139.80	1.60
				69.10	99.75	1.44
				51.15	77.60	1.52
				40.70	63.80	1.57
				27.05	54.20	2.00
				9.10	21.90	2.41
87.20	43.65	93.05	2.13	95.15	18.33	2.17
				60.05	94.20	1.55
				33.10	50.00	1.53
				22.60	31.00	1.42
				18.05	26.75	1.48
				16.35	26.40	1.61
				3.47	4.80	1.39
96.4	38.95	92.00	2.36	98.00	175.05	1.79
				68.35	98.20	1.44
				55.65	69.30	1.25
				42.50	53.80	1.27
				35.25	41.15	1.17
				31.35	37.45	1.19
				27.70	31.80	1.15
				25.55	29.70	1.16
				22.90	26.40	1.15
				7.97	12.05	1.51
				1.76	2.24	1.28

* Low molecular weight extract

Table S2. GAUSSIAN Archive Entries for the Optimized Geometries

CH₃CHClCH₂CHClCH₂CHClCH₂CH(Cl)•

```
1\1\GINC-SC71\FOpt\UmPWPW91\6-31+G(d,p)\C8H13Cl4(2)\MLC501\01-Jun-2004
\0\#\ MPWPW91\6-31+G** OPT=(MAXCYC=300) IOP(3/76=0572004280) MAXDISK=4
02653184\VC_tetra-prelim-mpw1k\0,2\Cl,-2.5695865753,-3.3382482879,2.
3573948676\C,-0.8625606226,-3.2721586671,2.3736123855\C,-0.194920893,-
1.9541902098,2.2945165674\C,-0.2665506117,-1.2784553687,0.9278470212\C
,0.3634493105,0.098932065,0.9518245033\H,-0.0996151516,0.6658366613,1.
7616408722\H,1.4236502451,-0.003533953,1.1902013969\C,0.251044355,0.89
57372641,-0.3323427468\H,-1.3005515995,-1.2164143093,0.6003509194\Cl,0
.556634256,-2.3092300231,-0.2924827661\H,0.8509845585,-2.0791806707,2.
5760208082\H,-0.6520672319,-1.2733393178,3.0159853829\H,-0.3707948243,
-4.1993045278,2.1353348763\C,0.989999756,2.2151327056,-0.2376039983\H,
0.6225049165,0.3150267504,-1.1716276056\Cl,-1.4857718277,1.2012182609,
-0.7029599169\C,1.0338855711,3.0385695034,-1.5087143888\H,0.5288209832
,2.8256691245,0.5409316131\H,2.0140492094,2.0064362831,0.0769284831\C,
1.6782640123,4.3879790577,-1.2961328742\Cl,1.9392361855,2.1417404765,-
2.7817807879\H,0.0318505921,3.155889577,-1.9108145759\H,1.7161453919,4
.9504485427,-2.2244646831\H,1.0976071733,4.959238329,-0.5727586973\H,2
.6930458161,4.2807821615,-0.9186813505\Version=DEC-AXP-OSF/1-G03RevB.
03\State=2-A\HF=-2153.4341067\S2=0.75623\S2-1=0.\S2A=0.750028\RMSD=7.2
60e-09\RMSF=4.970e-06\Dipole=0.6184122,0.9344894,1.2296965\PG=C01 [X(C
8H13Cl4)]\@
```

Intramolecular 1–2 Hydrogen Shift TS (1)

```
1\1\GINC-SC5\FTS\UmPWPW91\6-31+G(d,p)\C8H13Cl4(2)\MLC501\05-May-2005\0
\#\ MPWPW91\6-31+G** OPT=(TS,CALCFC,NOEIGENTEST,MAXCYC=300) IOP(3/76=0
572004280) MAXDISK=402653184\TS_12-teta-61+dpmpw1k\0,2\H,-4.68148394
96,-2.090698925,0.4753035367\C,-3.6049444542,-2.1167476753,0.519515954
8\C,-2.8685114164,-0.8431902033,0.4570332783\C,-1.4560264996,-0.742780
6455,0.0489605112\H,-3.4922258602,0.0360729523,0.3681339438\Cl,-1.3707
066436,-0.7071252561,-1.7811869605\H,-0.903161991,-1.6376055538,0.3177
107796\C,-0.7769045887,0.4955044875,0.5999414498\C,0.6966435443,0.6348
092343,0.2778789359\H,-0.9067578425,0.4903791538,1.6831625221\H,-1.289
3115826,1.3778651333,0.2134100299\H,-3.1210214994,-1.5055493209,1.5511
852294\Cl,-2.8959857062,-3.6040810051,0.0086833249\C,1.2565438578,1.94
45413542,0.794289261\Cl,1.6041083959,-0.7410393921,1.0082096282\H,0.86
19801911,0.5476812452,-0.791870472\C,2.7000987513,2.2329397033,0.43596
91739\H,0.6340153734,2.7528514943,0.4066235921\H,1.172188811,1.9629886
584,1.8825325201\C,3.2125956618,3.4928560365,1.092927917\Cl,2.86368554
69,2.3857630458,-1.3510166123\H,3.3258434102,1.3857704592,0.701090437\
H,4.241428175,3.689386034,0.8056801893\H,2.6081218739,4.3528639656,0.8
123439909\H,3.1746886724,3.380605281,2.1758753436\Version=Al64T-G03Re
vC.02\State=2-A\HF=-2153.3594805\S2=0.764188\S2-1=0.\S2A=0.750086\RMSD
=5.859e-09\RMSF=3.604e-06\Dipole=-0.8194492,1.102901,1.5605321\PG=C01
[X(C8H13Cl4)]\@
```

CH₃CHClCH₂CHClCH₂CHClCH•CH₂Cl

```
1\1\GINC-SC20\FOpt\UmPWPW91\6-31+G(d,p)\C8H13Cl4(2)\MLC501\05-May-2005
\0\#\ MPWPW91\6-31+G** OPT=(MAXCYC=300) IOP(3/76=0572004280) MAXDISK=4
02653184\12_prod-teta-61+dpmpw1k\0,2\Cl,-2.4630695926,-3.5076783166,
2.1732359083\C,-0.6507373947,-3.5488523654,2.05904869\C,-0.1006242746,
-2.1894252663,2.0030871579\C,0.0082723768,-1.4618429794,0.7279554292\C
,0.055446245,0.0404787372,0.9042233811\H,-0.8368886158,0.3297762163,1.
4621756916\H,0.922384909,0.2944320369,1.5163922189\C,0.1323302172,0.85
43315803,-0.3711099796\H,-0.7914201469,-1.7447578983,0.0480693942\Cl,1
.5261585804,-2.0323796989,-0.1244519667\H,0.2277239126,-1.7098502262,2
.9136620675\H,-0.3146165961,-4.0963119947,2.9311271364\H,-0.4291429992
,-4.1181708774,1.1619483581\C,0.2390649801,2.3370401748,-0.077711774\H
,0.971960036,0.5281215468,-0.9777448993\Cl,-1.3266129891,0.53968124,-1
.3797864236\C,0.4403385286,3.2336004834,-1.2822941158\H,-0.6674980251,
2.6640465346,0.4347709987\H,1.0730705807,2.48593659,0.6103988758\C,0.4
152085508,4.6989998832,-0.9171957903\H,-0.3112386534,3.0176745561,-2.0
359995405\Cl,2.0113249756,2.8450052852,-2.0731325963\H,0.5800158528,5.
3198541931,-1.7929907199\H,-0.5563650401,4.9529733088,-0.4949685373\H,
1.1836028485,4.9316098634,-0.1828687057\Version=Al64T-G03RevC.02\Stat
e=2-A\HF=-2153.4340393\S2=0.75799\S2-1=0.\S2A=0.750051\RMSD=9.877e-09\
RMSF=3.800e-06\Dipole=0.0658867,0.739205,1.1895947\PG=C01 [X(C8H13Cl4)
]\@
```

Intramolecular 1–2 Hydrogen Shift TS (dimer model) (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,CALCF,NOEIGENTEST,MAXCYC=300) IOP(3/76=
0572004280) MAXDISK=268435456\TS_12-cla-mpwlk\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\C1,1.094473310
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\C1,-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)]\@
```

CH₃CHClCH₂CH(Cl)•

```
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-alb3-mpwlk\0,2\C1\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\C1,4,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)]\@
```

CH₃CHClCH•CH₂Cl

```
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-mpwlk\0,2\C1,-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\C1,2.0545399648,-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)]\@
```

Intramolecular 1–3 Hydrogen Shift TS (2)

```
1\1\GINC-AC50\FTS\UmpWPW91\6-31+G(d,p)\C8H13Cl4(2)\MLC501\22-May-2006\
0\#\ MPWPW91/6-31+G** OPT=(TS,calcfc,noeigentest,maxcyc=300) IOP(3/76=
0572004280) INT(grid=ultrafine) maxdisk=402653184\TS_13-tet-alb1-61+d
pmpwlk\0,2\C,0.0065719765,-0.0010441953,-0.0022104914\C,-0.0016494925
,0.0028663806,1.5113164481\C,1.5176693743,-0.0003852518,1.5544633328\C
1,-0.7675286816,1.3043301439,-0.8555134203\H,-0.1722749191,-0.95438197
97,-0.4839710193\H,1.3807322717,0.0360921599,0.1801723224\H,-0.4661969
251,-0.8692149156,1.9611359116\H,-0.4403784322,0.9009712452,1.93939812
54\C1,2.2573527389,-1.4751484306,2.1526645094\C,2.1897536749,1.2642922
079,2.0043696534\H,1.6613747535,2.1014969449,1.5456352846\H,2.06473370
19,1.3587993404,3.0878583679\C,3.6704811119,1.3749533172,1.6980295506\
C,4.2630990052,2.6428860979,2.2794663357\H,4.1990658967,0.5048282318,2
.0764576612\C1,3.9252836238,1.3458198996,-0.0811164956\C,5.7638079456,
2.7926622769,2.1355122111\H,3.7937722451,3.5051574194,1.8022675353\H,4
.0100183563,2.6810620127,3.3404565283\C,6.2561790683,4.1340173954,2.62
48176762\C1,6.5951715381,1.4837112091,3.0529264233\H,6.0556173439,2.63
54036172,1.1012918131\H,7.3355005025,4.2094731157,2.529950561\H,5.8037
103223,4.926892994,2.0303892357\H,5.9920445716,4.2899493694,3.66870718
55\Version=IA64L-G03RevD.01\State=2-A\HF=-2153.3640492\S2=0.766951\S2
-1=0.\S2A=0.750115\RMSD=8.319e-09\RMSF=3.751e-07\Thermal=0.\Dipole=-0.
5675565,0.8208261,0.6709294\PG=C01 [X(C8H13Cl4)]\@
```

CH₃CHClCH₂CHClCH₂C•(Cl)CH₂CH₂Cl

1\1\GINC-SC74\FOpt\UmpWPW91\6-31+G(d,p)\C8H13Cl4(2)\MLC501\01-May-2005
\0\# MPWPW91/6-31+G** OPT=(MAXCYC=300) IOP(3/76=0572004280) MAXDISK=4
02653184\13_prod-tetb-61+dpmpw1k\0,2\Cl,-2.0692142782,-3.1635468045,
1.4009627085\Cl,-0.2886907264,-3.0609741943,1.6548808638\Cl,0.1131338899
, -1.6167510696,1.8748988637\Cl,-0.1380307781,-0.6789521789,0.7126795295
\Cl,0.1878010001,0.7656776523,1.0699323097\H,-0.383611213,1.002199691,1
.9730906595\H,1.2441094741,0.8412129525,1.3267399433\Cl,-0.1196149385,1
.7632235911,0.0147833289\H,-1.1691108771,-0.7568094296,0.3793939031\Cl
,0.8530148563,-1.1822077553,-0.7036634407\H,1.1764066705,-1.5994133143
,2.1215105981\H,-0.4272645496,-1.2325658861,2.7417916537\H,0.145502123
5,-3.4311317833,0.7307475818\Cl,0.8634594636,2.633776294,-0.6785726183\Cl
, -1.7829705875,1.9966789757,-0.3638813602\Cl,0.9487864386,2.344682494
4,-2.1688169366\H,0.6035749943,3.6857498786,-0.5411369511\H,-0.0072298
524,2.5036410147,-2.6553596655\Cl,2.1205323638,3.4357974885,-2.9548286
223\H,1.2795222077,1.3290567555,-2.3530385277\Cl,0.1017012518,-3.948050
4977,2.8132735279\H,1.8432440505,2.4808364085,-0.2296081296\H,1.184750
5929,-3.9390195283,2.9301800839\H,-0.3497422486,-3.6011355005,3.740379
718\H,-0.2145850037,-4.972686182,2.6409380738\Version=Al64T-G03RevC.0
2\State=2-A\HF=-2153.4376986\S2=0.757163\S2-1=0.\S2A=0.750038\RMSD=5.9
22e-09\RMSF=6.876e-06\Dipole=0.4433943,-0.3953026,1.4471516\PG=C01 [X(C8H13Cl4)]\@

Intramolecular 1–4 Hydrogen Shift TS (3)

1\1\GINC-SC82\FTS\UmpWPW91\6-31+G(d,p)\C8H13Cl4(2)\MLC501\08-Jun-2004\
0\# MPWPW91/6-31+G** OPT=(TS,CALCF,NOEIGENTEST,MAXCYC=300) IOP(3/76=
0572004280) MAXDISK=402653184\TS_1_4-alb2c3-mpw1k\0,2\Cl,-1.676118872
5,1.9289408491,-0.5501097759\Cl,-1.5129646561,2.0547203448,0.943714183\
Cl,0.0000363103,2.0540860059,1.1630256813\Cl,0.5621472855,1.0918290077,0
.1402424726\H,-0.4856909564,1.3131917632,-0.7146753253\Cl,-3.007133449
8,0.9629139779,-1.1206123595\H,-1.5966182324,2.8439417368,-1.123956982
9\H,-1.9352606312,1.1768321691,1.4321028081\H,-1.9974233852,2.93174872
86,1.3654290801\H,0.2761939744,1.8039434571,2.1829115042\Cl,0.66414582
45,3.6944976211,0.870149488\H,1.4885515806,1.3935310076,-0.3346133725\
Cl,0.4908375436,-0.3653919904,0.4630569997\H,-0.4962600222,-0.631548650
8,0.8320449934\Cl,1.596353255,-0.7267671688,1.8631868754\Cl,0.862495707
3,-1.2222068521,-0.7317510433\H,1.8560636091,-0.94064094,-1.076745281\
H,0.1608391694,-0.9814524345,-1.5321747791\Cl,0.8242306364,-2.720288179
, -0.485649365\Cl,1.3073424491,-3.5317391033,-2.0175107211\H,1.59137764
46,-2.9984430824,0.2301504831\Cl,-0.5204678656,-3.2461934788,-0.0434173
509\H,-1.3037592182,-2.9563964035,-0.7410782526\H,-0.5038728635,-4.330
167508,0.0231876257\H,-0.76735454,-2.8589046462,0.9441208799\Version=
DEC-AXP-OSF/1-G03RevB.03\State=2-A\HF=-2153.3884257\S2=0.764784\S2-1=0
.\S2A=0.750103\RMSD=5.535e-09\RMSF=3.463e-06\Dipole=-0.6655871,0.24167
67,0.4739591\PG=C01 [X(C8H13Cl4)]\@

CH₃CHClCH₂CHClCH•CHClCH₂CH₂Cl

1\1\GINC-SC69\FOpt\UmpWPW91\6-31+G(d,p)\C8H13Cl4(2)\MLC501\02-Jun-2004\
\0\# MPWPW91/6-31+G** OPT=(MAXCYC=300) IOP(3/76=0572004280) MAXDISK=4
02653184\14_prod-prelim-mpw1k\0,2\Cl,-2.3463984129,-3.5438160154,1.5
289762477\Cl,-0.7751971486,-3.3093065158,2.3428055684\Cl,-0.3274236812,-
1.8679328693,2.3032498478\Cl,-0.0569981445,-1.3105428268,0.9217746635\Cl
,0.3392905507,0.1058793611,0.9342893414\H,0.8229247325,0.5098524161,1.
8133074699\Cl,0.0934542526,0.9855269312,-0.2185560281\H,-0.9116446415,-
1.4713548183,0.2694911574\Cl,1.2871116844,-2.2699897874,0.1255268701\H
,0.5774940353,-1.7809827568,2.9069800638\H,-1.0901597057,-1.2393389519
,2.7638789358\H,-0.0641455673,-3.962234263,1.848605445\Cl,1.0557524846,
2.1508570679,-0.2974534693\Cl,-1.6253199933,1.6139400255,-0.0928840082\
Cl,0.8848809702,3.0698373494,-1.4892765995\H,0.95726577,2.752492241,0.
607783209\Cl,1.8241327811,4.2515405888,-1.4390722114\Cl,1.1668226013,2.
1497705054,-3.0115977688\H,-0.1456782401,3.4060105821,-1.5548213995\H,
1.695396022,4.886000006,-2.3111335086\H,1.6161923147,4.8456745254,-0.5
498860088\H,2.861250296,3.9248985541,-1.4027843504\H,-0.9061252195,-3.
6363553989,3.3684881219\H,2.0665475514,1.7397415779,-0.308842784\H,0.0
956603104,0.4220613912,-1.1479958205\Version=DEC-AXP-OSF/1-G03RevB.03
\State=2-A\HF=-2153.4345206\S2=0.758081\S2-1=0.\S2A=0.750052\RMSD=7.68
5e-09\RMSF=2.757e-06\Dipole=0.8238404,0.8093382,1.4116475\PG=C01 [X(C8H13Cl4)]\@

Intramolecular 1–5 Hydrogen Shift TS (4)

1\1\GINC-SC53\FTS\UmPWPW91\6-31+G(d,p)\C8H13Cl4(2)\MLC501\11-Jun-2004\0\#\ MPWPW91\6-31+G** OPT=(TS,CALCF,NOEIGENTEST,MAXCYC=300) IOP(3/76=0572004280) MAXDISK=402653184\TS_1_5-a2b2-mpwlk\0,2\C,-0.4358274391,1.9364617757,0.2199335529\C,-0.481111195,1.7886673777,1.7161113654\H,0.5311575288,1.7952319382,2.1187200465\C,-1.1488896938,0.4708454876,2.0811356029\H,-1.0171382887,2.6198992332,2.1751068632\C,-0.3906607682,-0.716633895,1.5089161313\H,-2.1807271357,0.4542393657,1.7389797966\C1,-1.2354324977,0.3214436837,3.8602906353\H,0.6284275244,-0.6990371745,1.8980874745\C,-0.3288008337,-0.6565418549,0.0021412804\H,-0.8483810292,-1.6498361905,1.8370257932\C1,-1.9005902861,-1.0382184626,-0.7270084408\C,0.8186577376,-1.4069624561,-0.6191869477\H,-0.2122241626,0.6680304755,-0.1704231978\C1,0.7988230226,3.017498004,-0.3764928239\H,-1.3840543686,2.1605422941,-0.2570397906\H,0.7804818335,-2.447827857,-0.2881352075\H,1.741099826,-0.983732191,-0.2184418282\C,0.8837573612,-1.3768077945,-2.1362427487\C,1.0148276054,0.0053367054,-2.726529923\H,0.0202364396,-1.8851255573,-2.5536078591\C1,2.2917667987,-2.3810656486,-2.6348332368\H,1.8759743382,0.528449218,-2.317019368\H,0.1212213447,0.5874242417,-2.5083240182\H,1.1245698669,-0.0486286728,-3.8058528614\Version=DEC-AXP-OSF/1-G03RevB.03\State=2-A\HF=-2153.4021895\S2=0.762884\S2-1=0.\S2A=0.750081\RMSD=7.343e-09\RMSF=9.721e-06\Dipole=-0.4040854,0.3035343,0.1286682\PG=C01 [X(C8H13Cl4)]\@

CH₃CHClCH₂C•(Cl)CH₂CHClCH₂CH₂Cl

1\1\GINC-SC33\FOpt\UmPWPW91\6-31+G(d,p)\C8H13Cl4(2)\MLC501\01-Jun-2004\0\#\ MPWPW91\6-31+G** OPT=(MAXCYC=300) IOP(3/76=0572004280) MAXDISK=402653184\15_prod-prelim-mpwlk\0,2\C1,-2.440621198,-3.3542309978,1.9370851138\C,-0.6590893241,-3.3824433193,2.0593901892\C,-0.0791661224,-1.9923979641,2.168007431\C,-0.2742541858,-1.1174349839,0.9453309356\C,0.2287085104,0.2954712962,1.1858871079\H,-0.2633503594,0.657642966,2.0981819353\H,1.2981251715,0.2633433374,1.393926443\C,0.0014980529,1.2614464184,0.0791530854\H,-1.3233063678,-1.0979627624,0.6638805737\C1,0.5805636249,-1.8326991956,-0.4605200988\H,0.9887554599,-2.0914961384,2.3707535395\H,-0.5273204764,-1.4862942172,3.0239513964\H,-0.2911383176,-3.8998587931,1.1800614061\C,0.874000368,2.4459261372,-0.1340963334\C1,-1.6202303754,1.4043141876,-0.4956548975\C,1.0740449673,2.8617787747,-1.582471269\H,0.4537843973,3.3122739863,0.3919415727\C,1.8271252151,4.1655778567,-1.7044475186\C1,1.9584803728,1.5713582563,-2.46309006\H,0.112285737,2.9334225101,-2.080426075\H,1.9753616087,4.4297714708,-2.7474276737\H,1.2610672446,4.9637685365,-1.2254766812\H,2.802756485,4.0981706401,-1.2273681035\H,-0.4202760998,-3.965212007,2.9423011959\H,1.847836579,2.2462669166,0.3122377251\Version=DEC-AXP-OSF/1-G03RevB.03\State=2-A\HF=-2153.4347513\S2=0.756357\S2-1=0.\S2A=0.750031\RMSD=8.501e-09\RMSF=1.211e-05\Dipole=0.6489769,1.0169509,1.3752751\PG=C01 [X(C8H13Cl4)]\@

Intramolecular 1–6 Hydrogen Shift TS (5)

1\1\GINC-SC71\FTS\UmPWPW91\6-31+G(d,p)\C8H13Cl4(2)\MLC501\09-Jun-2004\0\#\ MPWPW91\6-31+G** OPT=(TS,CALCF,NOEIGENTEST,MAXCYC=300) IOP(3/76=0572004280) MAXDISK=402653184\TS_1_6-prelim5-mpwlk\0,2\C,-0.5871427054,-1.331619943,-1.2729561841\C,0.9120083301,-1.3717719315,-1.2730118813\C,1.5657890812,0.0023609354,-1.2494065971\C,1.4240986492,0.7997758746,0.044585018\C,0.043811622,1.4137673969,0.264181316\C,-1.107803222,0.4974183182,0.5711388077\H,-0.9252876276,-0.4938854952,-0.2992532601\H,-1.0785419437,-2.2641155649,-1.0247348543\H,1.2398645214,-1.9383063361,-0.4006121672\H,1.2635206178,-1.9130007973,-2.1518674191\C1,3.3233668511,-0.2317605866,-1.544497792\H,1.2151604977,0.5911404437,-2.0940395865\H,2.1306317424,1.6243712285,-0.004866474\H,1.7237751924,0.1814138724,0.8864743676\H,-0.2187009415,1.9814364177,-0.6250613232\C1,0.1918194774,2.6804719697,1.5561676222\H,-2.0485162358,0.9077550665,0.2159674383\C,-1.2828104546,-0.1046597233,1.9412094979\H,-1.6379205536,0.6705083755,2.6178622151\C1,-2.6585191723,-1.2702909679,1.8427307591\C,-0.0933569111,-0.7976099635,2.5623388839\H,-0.3790647051,-1.2440727031,3.510486517\H,0.69422926,-0.0735987099,2.7586187563\H,0.2930990472,-1.5859434531,1.9206302594\C1,-1.2990092273,-0.6542832463,-2.7272286855\Version=DEC-AXP-OSF/1-G03RevB.03\State=2-A\HF=-2153.3948739\S2=0.762442\S2-1=0.\S2A=0.750081\RMSD=6.420e-09\RMSF=6.918e-06\Dipole=0.167775,-0.2809941,0.1984381\PG=C01 [X(C8H13Cl4)]\@

CH₃CHClCH₂CHClCH₂CHClCH₂CH₂Cl

1\1\GINC-SC51\FOpt\UmpWPW91\6-31+G(d,p)\C8H13Cl4(2)\MLC501\01-Jun-2004
\0\# MPWPW91/6-31+G** OPT=(MAXCYC=300) IOP(3/76=0572004280) MAXDISK=4
02653184\16_prod-prelim-mpw1k\0,2\Cl,-2.6129467873,-3.0436636082,2.3
683890907\C,-0.8462015533,-3.2920217391,2.3023987347\C,-0.0985593919,-
1.9899149607,2.1402585527\C,-0.346666928,-1.2616313682,0.8342771558\C,
0.3536535256,0.0812019677,0.8051255719\H,0.0286898136,0.6477268362,1.6
793742541\H,1.4303605923,-0.0729335047,0.8951939217\C,0.1229761645,0.9
206733116,-0.4328667731\H,-1.4130143134,-1.1353832286,0.6704203847\Cl,
0.2234866512,-2.2745636756,-0.5407472045\H,0.967708711,-2.2024078464,2
.2364342471\H,-0.3714491357,-1.3193475949,2.9559592102\H,-0.653807948,
-3.9682570904,1.4765094145\C,0.8562724945,2.1954789386,-0.4121167379\H
,0.3540790853,0.3533695874,-1.330695655\Cl,-1.6648158895,1.2926414925,
-0.6013509251\C,1.2187028471,2.8952544985,-1.6542357852\H,1.1345110974
,2.6322691575,0.5372454181\C,1.4087341425,4.3826962442,-1.4911504616\C
1,2.7737382515,2.1612340858,-2.2922306359\H,0.4976423098,2.6786590947,
-2.4383852477\H,1.7132028324,4.8401993657,-2.4277922183\H,0.4684832244
,4.8310167308,-1.173691813\H,2.1670473711,4.5958503195,-0.7412516749\H
, -0.5677792876,-3.7772041874,3.2315126875\Version=DEC-AXP-OSF/1-G03Re
vB.03\State=2-A\HF=-2153.4346335\S2=0.758094\S2-1=0.\S2A=0.750052\RMSD
=5.522e-09\RMSF=4.103e-06\Dipole=0.6810523,0.6354219,1.0193555\PG=C01
[X(C8H13Cl4)]\@

CH₃CHClCH₂CHClCH₂CHClCH₂CH₂Cl

1\1\GINC-AC29\FOpt\UmpWPW91\6-31+G(d,p)\C8H13Cl4(2)\EXK501\29-Nov-2005
\0\# MPWPW91/6-31+G** OPT=TIGHT FREQ=NORAMAN IOP(3/76=0572004280) MAX
DISK=134217728\16_PVCTri+HTH-12Clprod\0,2\H,1.7372529254,-0.0630547219,
0.8075462706\C,1.5660414557,0.4432068791,-0.1391092817\Cl,1.2614283555
,2.1830981973,0.3468309534\C,0.3420179221,-0.1154297908,-0.8319223465\
C,-0.9295641403,-0.142657369,-0.0090414491\H,0.5851623921,-1.130252195
7,-1.1517318418\H,0.1476571057,0.4741597813,-1.7293786786\H,-1.1475190
663,0.8464320922,0.3828663183\Cl,-0.689698374,-1.1812661169,1.44304797
95\C,-2.1025977716,-0.6592615442,-0.8171452003\C,-3.4490846518,-0.6169
515888,-0.1239707487\H,-1.907365378,-1.693733763,-1.1055711504\H,-2.16
48953697,-0.0722072598,-1.7351489079\Cl,-3.8978204634,1.091603216,0.22
80200937\H,-3.3807796109,-1.092738874,0.8499586041\C,-4.5393750634,-1.
2586920254,-0.9490588777\H,-5.4969324603,-1.1995014569,-0.4399141881\H
, -4.3024687015,-2.309371869,-1.1124123299\H,-4.6351828175,-0.770640949
7,-1.9167394113\C,2.7724610979,0.4088424016,-0.9820490388\C,4.11518120
01,0.4151915208,-0.3897042631\H,4.1529696679,0.9829059538,0.534583588\
H,4.8687459136,0.7832242131,-1.0751919099\Cl,4.6336480331,-1.268483721
4,0.0526596111\H,2.6643967362,0.375111375,-2.05635597\Version=IA64L-G
03RevC.02\State=2-A\HF=-2153.4340394\S2=0.75799\S2-1=0.\S2A=0.750051\R
MSD=5.411e-09\RMSF=1.612e-06\Dipole=-0.1350587,-0.4195601,-1.3308619\PG
=C01 [X(C8H13Cl4)]\@

TS: Intramolecular 1-5 Hydrogen transfer in CH₃CHClCH₂CHClCH₂CHClCH₂CH₂Cl (6)

1\1\GINC-AC47\FTS\UmpWPW91\6-31+G(d,p)\C8H13Cl4(2)\EXK501\08-Dec-2005\
\0\# MPWPW91/6-31+G** OPT=(TS,CALCF,NOEIGENTEST,MAXCYC=300) IOP(3/76=
0572004280) MAXDISK=134217728\16_PVCTri+HTH-12Clprod-15H-e\0,2\C,-0.
4365185802,-0.0946495253,1.2745129206\C,1.0478835952,0.0652890172,1.30
54775579\H,1.3216428794,1.1137803537,1.233424901\C,1.7028667141,-0.724
3114671,0.1875676845\Cl,1.7145479885,-0.4844684106,2.895236238\C,1.234
9864124,-0.2566498473,-1.1896355346\H,1.4460016668,-1.7799640722,0.297
5286396\H,2.7847624642,-0.6477945977,0.2521562915\Cl,1.8931326831,1.37
67189043,-1.5337705551\C,-0.2717029038,-0.2518759295,-1.3230866042\H,1
.6926558419,-0.898092524,-1.9412620768\C,-0.8754139428,-1.5664909627,-
1.7309648012\H,-0.6809832717,0.5961395433,-1.8609108466\H,-0.622632224
4,-0.0522114296,-0.0476157139\C,-1.2937730154,0.9189172272,1.958273410
4\H,-0.7577370802,-1.1080803341,1.5068621793\Cl,-1.0616376293,2.567258
3619,1.3086844161\H,-2.3438529301,0.677319153,1.8366522255\H,-1.065422
8457,0.9739094477,3.0212379585\Cl,-2.613713358,-1.5913360619,-1.255583
6365\C,-0.7711569502,-1.8428561639,-3.2166588098\H,-0.4257805014,-2.38
26713781,-1.1687602111\H,-1.2175153939,-2.8026707882,-3.4628549612\H,-
1.2781682563,-1.0679471046,-3.7860345743\H,0.2743970437,-1.8648878543,
-3.5209686144\Version=IA64L-G03RevC.02\State=2-A\HF=-2153.3970658\S2=
0.762981\S2-1=0.\S2A=0.750089\RMSD=7.764e-09\RMSF=4.529e-06\Dipole=0.0
765664,-1.1946021,-0.674088\PG=C01 [X(C8H13Cl4)]\@

CH₃CHClCH₂CHClCH₂CHClCHClCH₂•

1\1\GINC-AC27\FOpt\UmPWPW91\6-31+G(d,p)\C8H13Cl4(2)\EXK501\24-Jul-2006
\0\# MPWPW91/6-31+G** OPT IOP(3/76=0572004280) MAXDISK=134217728\PVC
HHtet-12-SM_a2b1\0,2\C,-3.7870935244,-2.0303626402,0.4299432521\C,-2.
3212295619,-2.0787422537,0.3934637119\C,-1.6338132334,-0.7303830976,0.
2565116323\C1,-1.7961173078,-3.2191550687,-0.9357884754\H,-1.930533467
5,-2.5449222041,1.2953136274\H,-1.9559161896,-0.1389122178,1.111270162
6\C1,-2.2130984284,0.1624810277,-1.1815423983\C,-0.1217064121,-0.82377
48141,0.2396177104\C,0.5999739376,0.4994351009,0.3919889364\H,0.192827
7319,-1.2787079257,-0.698577028\H,0.1878278759,-1.4933139246,1.0442778
539\C1,0.2144991211,1.2191798179,2.0011926588\H,0.2330085343,1.2191756
98,-0.3340119369\C,2.099413852,0.3341207828,0.2542035882\C,2.912666825
7,1.6118129376,0.2957574841\H,2.2939236299,-0.1733964731,-0.6921112898
\H,2.4607016625,-0.3175457417,1.0519274195\H,2.6548074675,2.1885952182
,1.1791885165\C1,2.460012385,2.667471024,-1.0914192855\C,4.3988988209,
1.3453903046,0.2555826224\H,4.9602445785,2.275039821,0.2713580269\H,4.
6726569705,0.7947594122,-0.641906903\H,4.6873441136,0.7561591033,1.125
3001208\H,-4.3285254196,-2.8321192841,0.9044204873\H,-4.3210598009,-1.
3293950193,-0.1903851764\Version=IA64L-G03RevC.02\State=2-A\HF=-2153.
4275951\S2=0.756735\S2-1=0.\S2A=0.750032\RMSD=6.055e-09\RMSF=1.129e-05
\Dipole=0.4856408,-0.7451498,0.9933537\PG=C01 [X(C8H13Cl4)]\@

Intramolecular 1–2 Chlorine Shift TS (7)

1\1\GINC-AC43\FTS\UmPWPW91\6-31+G(d,p)\C8H13Cl4(2)\EXK501\24-Jul-2006\
0\# MPWPW91/6-31+G** OPT=(TS,CALCF,NOEIGENTEST,MAXCYC=200) IOP(3/76=
0572004280) MAXDISK=134217728\PVCHtet-12-TS_a2b1c1\0,2\C,-3.6657374
168,-2.1572418193,-0.1110344656\C,-2.4886994488,-1.7910539626,-0.67131
16604\C,-1.7442138485,-0.5199718125,-0.4351084228\C1,-1.6319299976,-3.
4917527116,0.9526551778\H,-2.1093766038,-2.3641147438,-1.5075360376\H,
-1.9405254564,0.1087884087,-1.3055446474\C1,-2.3730996143,0.401553721,
0.9573233988\C,-0.2432850961,-0.7196486494,-0.3108544126\C,0.571336945
3,0.552795154,-0.4141214673\H,-0.037214559,-1.1957822152,0.6458804498\
H,0.0746944105,-1.4152607852,-1.0885263063\C1,0.3432368009,1.286067432
1,-2.0475625078\H,0.2048796328,1.3003902168,0.2834460131\C,2.042990368
8,0.288638184,-0.1720933737\C,2.941653161,1.508426807,-0.1649428452\H,
2.1362390651,-0.2205498888,0.7885435927\H,2.4133837958,-0.3949284587,-
0.938242532\H,2.7901278482,2.0881066711,-1.0708340891\C1,2.4596976286,
2.6128761865,1.173725725\C,4.3991463986,1.1436759718,-0.0100399543\H,5
.0220638552,2.033234641,0.006354326\H,4.567008317,0.5903421639,0.91147
97376\H,4.7108010754,0.5224117296,-0.8488992046\H,-4.1754151296,-3.043
650656,-0.4508735945\H,-4.1001945325,-1.5913649983,0.6973814081\Versi
on=IA64L-G03RevC.02\State=2-A\HF=-2153.4096939\S2=0.760802\S2-1=0.\S2A
=0.750041\RMSD=5.059e-09\RMSF=9.095e-06\Dipole=0.1121558,-0.3852751,-1
.0892684\PG=C01 [X(C8H13Cl4)]\@

CH₃CHClCH₂CHClCH₂CHClCH•CH₂Cl

1\1\GINC-AC27\FOpt\UmPWPW91\6-31+G(d,p)\C8H13Cl4(2)\EXK501\24-Jul-2006
\0\# MPWPW91/6-31+G** OPT IOP(3/76=0572004280) MAXDISK=134217728\PVC
HHtet-12-prod_alb2\0,2\C,-3.4600109158,-2.2992450237,-0.0197465491\C,
-2.0940631244,-2.0549037942,0.4580358435\C,-1.4255694819,-0.7630727107
,0.2311583864\H,-1.7570414653,-0.3107609442,-0.7001390434\C1,-2.003980
4315,0.4094865089,1.5143725875\C,0.0840875013,-0.8609849483,0.27184641
71\C,0.8380621497,0.4268525259,0.0114595069\H,0.3848146437,-1.23271328
12,1.2527635937\H,0.3807774645,-1.6071241748,-0.4674186348\C1,0.445515
3313,1.0362226902,-1.6375854905\H,0.5011635408,1.2057921638,0.68906381
04\C,2.334914426,0.2290693146,0.1389011442\C,3.1775206094,1.4818964852
,0.0134040725\H,2.5336195933,-0.2284705289,1.1096829542\H,2.6667556486
, -0.4750955442,-0.6262595628\H,2.9105906952,2.020168648,-0.8913555122\
C1,2.7848193269,2.6153624349,1.3570711421\C,4.6577037801,1.1817609233,
0.0311503753\H,5.2397804889,2.0958562382,-0.0414054543\H,4.9407653221,
0.667187732,0.94704857\H,4.911030489,0.5459807816,-0.8164021234\H,-4.0
667996147,-1.3994626544,-0.004824555\C1,-3.4497121233,-2.849752432,-1.
7506803078\H,-3.9585758483,-3.0849533117,0.5346040477\H,-1.5656663829,
-2.8370681906,0.9833618961\Version=IA64L-G03RevC.02\State=2-A\HF=-215
3.4340394\S2=0.75799\S2-1=0.\S2A=0.750051\RMSD=4.294e-09\RMSF=2.036e-0
6\Dipole=0.7950712,-1.1067086,0.3289561\PG=C01 [X(C8H13Cl4)]\@

2nd Intramolecular 1–2 Chlorine Shift TS (8)

1\1\GINC-AC25\FTS\UmpWPW91\6-31+G(d,p)\C8H13Cl4(2)\MLC501\09-Aug-2007\0\#\ MPWPW91\6-31+G** IOP(3/76=0572004280) OPT=(TS,calcfc,noeigentest,maxcyc=200) INT(grid=ultrafine) maxdisk=671088640\2nd_Cl_TS-geom\0,2\C,0.1184649365,-0.0547656576,-0.1442018732\C,1.4517736831,-0.214104711,0.055068988\C,2.4346448286,0.8998058997,-0.0059387421\Cl,0.4952489531,0.0018692641,2.4179016454\H,1.8452201583,-1.2165015041,0.1662846127\H,2.8052733215,0.9617150759,-1.0334513889\C,3.6234176751,0.7573165972,0.9290017019\C,4.5289392662,1.9693551663,0.8589938765\H,3.2791074921,0.5919935183,1.9455528621\Cl,4.5517777644,-0.7233442137,0.492004926\H,3.9208421705,2.8539431391,1.0563439415\C,5.7069477823,1.9706135434,1.8120649799\C,6.6138982646,3.1593702342,1.5970441162\Cl,5.1150125946,1.9723958032,3.5112544897\H,6.2663948624,1.0450536691,1.7123094018\H,7.0233622167,3.1288900357,0.5879652795\C,-0.8338535622,-1.1880292361,-0.2159860962\H,-0.2872980045,0.9357574787,-0.3013965147\H,-1.7038542384,-1.0116774295,0.4059397265\Cl,-1.4269294126,-1.3628874805,-1.8971438511\H,-0.3694595659,-2.1249578369,0.0687294781\H,1.9329556528,1.8417038733,0.2146194614\H,4.9204740249,2.0628513468,-0.1558663831\H,6.0698471601,4.0931858406,1.722350582\H,7.4404519758,3.1481675839,2.30150478\Version=IA64L-G03RevD.01\State=2-A\HF=-2153.4151422\S2=0.75531\S2-1=0.\S2A=0.750017\RMSD=2.430e-09\RMSF=2.889e-06\Thermal=0.\Dipole=0.509835,0.8315464,-1.194785\PG=C01 [X(C8H13Cl4)]\@

CH₃CHClCH₂CHClCH₂CH•CHClCH₂Cl

1\1\GINC-AC42\FOpt\UmpWPW91\6-31+G(d,p)\C8H13Cl4(2)\MLC501\17-Aug-2007\0\#\ MPWPW91\6-31+G** IOP(3/76=0572004280) OPT INT(grid=ultrafine) maxdisk=671088640\2nd_Cl_prod-geom\0,2\H,0.0091031462,0.0537613315,-0.008163656\C,0.0074638371,0.0014734292,1.0766817269\C,1.4155942908,0.040368579,1.6212862447\C,1.4515956976,-0.0577222184,3.1325082079\C,2.8173486463,0.0902127012,3.7709548994\C,2.768641956,-0.1492447577,5.2698633417\C,4.0893212857,-0.1125804324,5.9419895631\C,4.2982299762,-0.7606459653,7.2391830103\C,5.7472169403,-0.9833003927,7.6067918434\H,6.3106124322,-0.0586880717,7.5374233967\Cl,6.4899921881,-2.1586846027,6.4951441206\H,5.8340288267,-1.3845062781,8.6093176305\Cl,3.6032146591,0.2896168719,8.5818344826\H,3.7393823201,-1.6888357104,7.3227554649\H,4.8365144058,0.5877647228,5.5960200016\H,2.0951350544,0.587495059,5.7235841293\H,2.303384833,-1.1248698979,5.4320536836\Cl,3.4635350239,1.7383560948,3.4380510482\H,3.5260753975,-0.589008769,3.3052440175\H,1.0428943758,-1.0254864247,3.4285141392\H,0.788949204,0.7106603291,3.5347189751\C,1.2.3679863914,-1.3104474915,0.9026615826\H,1.9241732068,0.9426171933,1.2944365277\H,-0.501632652,-0.9125295652,1.375215814\H,-0.5545148979,0.852327137,1.4599879379\Version=IA64L-G03RevD.01\State=2-A\HF=-2153.4330781\S2=0.757131\S2-1=0.\S2A=0.750038\RMSD=8.786e-09\RMSF=1.014e-06\Thermal=0.\Dipole=-0.9686879,0.0140667,0.1983771\PG=C01 [X(C8H13Cl4)]\@

Intramolecular 1–5 Chlorine Shift TS (9)

1\1\GINC-AC58\FTS\UmpWPW91\6-31+G(d,p)\C8H13Cl4(2)\EXK501\15-Sep-2006\0\#\ MPWPW91\6-31+G** OPT=(TS,CALCFC,NOEIGENTEST,MAXCYC=200) IOP(3/76=0572004280) MAXDISK=134217728\ts_PVCtet-15Cl_a2b2c1\0,2\C,-0.7776198421,1.2588056522,2.2259537779\C,0.7152958764,1.1178765412,2.3096147811\H,1.1599260222,2.102856054,2.169833631\C,1.3623150753,0.1315937697,1.3160513424\H,0.9644355902,0.7940316299,3.3190349892\C,1.7406585649,0.6715368463,-0.0805908381\H,0.7476040632,-0.7610845894,1.234236187\Cl,2.8958635362,-0.4340854852,2.0805651116\H,2.1477093207,1.6739613713,0.0432307461\C,0.6723103932,0.6808030827,-1.1423364512\H,2.5580587072,0.0497141074,-0.4499807922\Cl,-0.9236705373,1.3597455842,0.1464566026\H,-1.1928749785,2.188371797,2.587681915\Cl,-1.6832235626,-0.0968949336,2.8242374854\C,0.2484008193,-0.6369923695,-1.7080049548\C,-0.9462173659,-0.5648441759,-2.6436081897\H,1.093302875,-1.070176633,-2.2553773033\H,0.0185302502,-1.33138059,-0.9007310462\Cl,-1.3579633969,-2.2432695437,-3.1482386525\C,-0.7247855368,0.2797101703,-3.8758352885\H,-1.5880240339,0.2321069692,-4.5334080725\H,-0.5774299379,1.321677406,-3.596905026\H,0.1475988727,-0.0616676217,-4.4297297255\H,-1.8170501819,-0.2158936982,-2.0959325493\H,0.7689628537,1.4931211269,-1.8507673278\Version=IA64L-G03RevC.02\State=2-A\HF=-2153.362965\S2=0.786741\S2-1=0.\S2A=0.75029\RMSD=2.742e-09\RMSF=3.589e-06\Dipole=0.4674902,1.284199,-0.2090531\PG=C01 [X(C8H13Cl4)]\@

CH₃CHClCH₂CH•CH₂CHClCH₂CHCl₂

1\1\GINC-AC22\FOpt\UmpWPW91\6-31+G(d,p)\C8H13Cl4(2)\MLC501\01-Oct-2006
0\#\# MPWPW91/6-31+G** OPT=(maxcyc=300) IOP(3/76=0572004280) maxdisk=6
71088640\c11_5prod-test2-mpw\0,2\H,0.0411731865,-0.0444546229,0.0747
269922\C,1.1253163994,-0.0219503962,0.0113871445\C,1.6422248979,1.3967
287756,0.0435651894\C,3.1539104796,1.4738726372,-0.0651304417\C,3.7242
493642,2.8342288221,0.1021498857\C,5.1846915152,3.0017232799,0.3122391
737\C,5.5934914008,4.360946677,0.8511078968\C,7.0744455772,4.411660510
1,1.1710417642\C,7.5433785226,5.7079135713,1.7909419243\H,7.30939809,6
.5612353397,1.1673558472\H,3.1439488559,3.685878608,-0.2227637094\H,1.
530088294,-0.5779774787,0.8564282287\H,1.4253950414,-0.5224863442,-0.9
068066432\C1,0.8825452813,2.33184465,-1.2953850482\H,1.3136656359,1.89
92786564,0.949923379\H,3.5670443141,0.8046273954,0.6962497523\H,3.4505
112857,1.0419293089,-1.0298900401\H,5.5411230603,2.2508071049,1.023804
5296\H,5.7367977058,2.8162883742,-0.6184002784\H,5.0057954826,4.602833
708,1.7322084878\C1,5.193108449,5.6455865705,-0.343945879\H,7.31200614
63,3.5970390792,1.8548235753\H,7.6476529144,4.2559250335,0.2578587788\
C1,9.3062542784,5.6800164678,1.979808675\C1,6.7571238214,5.9980442723,
3.3559808153\Version=IA64L-G03RevD.01\State=2-A\HF=-2153.4243836\S2=0
.755695\S2-1=0.\S2A=0.750023\RMSE=4.745e-09\RMSE=2.137e-06\Thermal=0.\
Dipole=0.1028929,-1.3968712,0.2917909\PG=C01 [X(C8H13Cl4)]\@

CH₂=CHCl

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\C1,0.2870193711,0.,1.018875563\Ve
rsion=DEC-AXP-OSF/1-G03RevB.03\State=1-A\HF=-538.1761332\RMSE=2.411e-
09\RMSE=2.466e-05\Dipole=-0.0510812,0.,-0.6300194\PG=CS [SG(C2H3Cl1)]\
@\

CH₃CHClCH•CHClCH₂CH₂Cl

1\1\GINC-AC44\FOpt\UmpWPW91\6-31+G(d,p)\C6H10Cl3(2)\EXK501\10-Aug-2006
0\#\# MPWPW91/6-31+G** OPT IOP(3/76=0572004280) MAXDISK=134217728\mid
chaintri-betaCl-SM_alb1\0,2\H,-0.5796943182,2.9561015281,-1.098793030
4\C,-0.3127301187,2.8403925923,-0.0540495823\C1,1.4648970026,2.9713733
99,0.0435202273\C,-0.8154458811,1.5318734218,0.5067972498\H,-0.7157697
009,3.6736637635,0.5110868845\C,-0.3560475945,0.2907079631,-0.22761745
04\H,-1.9062244801,1.5638057578,0.5068154795\H,-0.4909113006,1.4337671
967,1.543231825\H,0.7269004483,0.2810220843,-0.323621299\C1,-0.9423385
558,0.3541820651,-1.9667274388\C,-0.8453550395,-0.9579749829,0.3749300
59\C,-0.1486724041,-2.2378119443,0.1725566031\C1,1.1968770975,-2.36017
56737,1.4115500356\H,0.3806427207,-2.2376381297,-0.776842053\C,-1.0392
935423,-3.4494695471,0.2936727148\H,-0.4672949754,-4.3650302569,0.1758
204764\H,-1.8019011613,-3.4126937368,-0.4828081232\H,-1.5307318145,-3.
4727486172,1.2636054305\H,-1.7401521897,-0.9380110432,0.9819388353\Ve
rsion=IA64L-G03RevC.02\State=2-A\HF=-1615.209762\S2=0.758085\S2-1=0.\S
2A=0.750052\RMSE=5.819e-09\RMSE=6.253e-06\Dipole=-1.2421378,-0.1176279
0.2427665\PG=C01 [X(C6H10Cl3)]\@

TS: β-Cl Elimination from Mid-Chain Radical (10)

1\1\GINC-AC52\FTS\UmpWPW91\6-31+G(d,p)\C8H13Cl4(2)\EXK501\28-Aug-2006\
0\#\# MPWPW91/6-31+G** OPT=(TS,CALCFC,NOEIGENTEST,MAXCYC=200) IOP(3/76=
0572004280) MAXDISK=134217728\midchaintri-betaCl-TS_start\0,2\H,-0.1
872051956,0.5847146684,2.1587143271\C,0.8427712634,0.6996246884,2.4759
292054\C1,1.1767002714,2.4549310601,2.528206848\C,1.7900642007,-0.0286
236217,1.5465102509\H,0.9530175497,0.337924601,3.4924174191\C,1.676644
9269,0.3521111391,0.1095314579\H,1.6178020211,-1.0991289316,1.66184261
54\H,2.8142215253,0.1667858849,1.8736191396\H,1.5634940389,1.407711726
8,-0.106677017\C1,-1.0862837094,-0.2325257779,-0.3432276272\C,1.806792
4963,-0.5091511701,-0.9085634977\C,1.8233725612,-0.1003230484,-2.33805
52084\C1,3.5492908257,-0.1221036765,-2.8994297906\H,1.513252759,0.9358
767632,-2.4341970783\C,1.007354451,-0.9958394243,-3.2395102665\H,1.083
8074062,-0.6714370492,-4.2735362011\H,-0.0341892728,-0.9588010378,-2.9
287500835\H,1.3540364196,-2.0248831556,-3.1756549477\H,1.9513219695,-1.
5649394462,-0.710999074\C,-3.6620333973,0.0486637343,-0.3393571069\C
,-3.9889369455,-1.1122047753,0.2404303382\H,-3.5693392112,0.9614912669
0.2260251176\H,-3.6246695336,0.1048496727,-1.4151606127\C1,-4.1741061
881,-1.2930924636,1.9298278454\H,-4.1269482083,-2.0282655107,-0.310547
4936\Version=IA64L-G03RevC.02\State=2-A\HF=-2153.3643901\S2=0.773698\
S2-1=0.\S2A=0.75021\RMSE=8.661e-09\RMSE=2.466e-06\Dipole=-1.0201015,-0
.7790964,-0.1171113\PG=C01 [X(C8H13Cl4)]\@

CH₃CHClCH=CHCH₂CH₂Cl

1\1\GINC-AC42\FOpt\RmPWPW91\6-31+G(d,p)\C6H10Cl2\EXK501\29-Aug-2006\0\0\# MPWPW91/6-31+G** OPT IOP(3/76=0572004280) MAXDISK=134217728\midcha intri-betaCl-prod_alb3c1d1\0,1\H,-0.6120543464,1.9808100693,1.2959082 936\C,0.470371817,2.0550901213,1.2982721165\C1,0.8744218095,3.79262415 73,1.3044403822\C,1.070464534,1.3519890627,0.0964697831\H,0.8473579023 ,1.6438547593,2.2297620919\C,0.7804794,-0.1123552019,0.1454341205\H,2. 1480733733,1.5200671177,0.0935703967\H,0.6721007398,1.78870741,-0.8173 973818\C,0.0303159758,-0.7630194328,-0.73516586\C,-0.22382985,-2.22726 67301,-0.6817053224\C1,-1.9899151728,-2.5073478571,-0.4039220992\H,0.2 666406329,-2.6601116991,0.1857419178\C,0.1946778547,-2.947064267,-1.94 42087041\H,-0.0277484764,-4.0085748465,-1.8779387373\H,1.2661478901,-2 .8215440812,-2.0916647746\H,-0.3230360293,-2.5405787963,-2.8100321267\ H,-0.4242572406,-0.2317743772,-1.5638617203\H,1.2152843408,-0.66479397 41,0.9725244282\Version=IA64L-G03RevC.02\State=1-A\HF=-1155.0281809\R MSD=8.819e-09\RMSF=1.318e-05\Dipole=0.729855,-0.6669873,-0.2399462\PG=C01 [X(C6H10Cl2)]\@

ClCH₂CH(Cl)•

1\1\GINC-AC58\FOpt\UmPWPW91\6-31+G(d,p)\C2H3Cl2(2)\EXK501\07-Sep-2006\ 0\0\# MPWPW91/6-31+G** OPT IOP(3/76=0572004280) MAXDISK=134217728\C1CH 2-CHClrad_al\0,2\C1,0.312430299,0.7880102086,-1.9708338154\C,0.439012 6456,0.4806577276,-0.3004794522\C,-0.2069285598,-0.7374352193,0.229693 7258\H,0.3892065454,-1.6329448276,0.0527089166\H,-1.1861831844,-0.8838 169224,-0.2167598856\C1,-0.4195795123,-0.6079375756,1.9923678109\H,1.2 260087505,0.99619194,0.2226874038\Version=IA64L-G03RevC.02\State=2-A\ HF=-998.3568986\S2=0.756177\S2-1=0.\S2A=0.750028\RMSD=3.973e-09\RMSF=1 .756e-05\Dipole=0.1864707,-0.2534344,-0.286971\PG=C01 [X(C2H3Cl2)]\@

CH₃CH•CH₂CH₂Cl

1\1\GINC-AC49\FOpt\UmPWPW91\6-31+G(d,p)\C4H8Cl1(2)\EXK501\25-Nov-2005\ 0\0\# MPWPW91/6-31+G** OPT=TIGHT FREQ=NORAMAN IOP(3/76=0572004280) MAXD ISK=134217728 MAXDISK=134217728\CH3CHCH2CH2Cl\0,2\C1,1.8909260584,-0 .522850789,0.090964\C,0.8772559,0.8962610979,-0.303255\C,-0.5088650884 ,0.7922519432,0.291693\C,-1.3388739656,-0.3082371494,-0.261349\C,-2.79 15029587,-0.3697503115,0.029649\H,-2.9857919259,-0.6635373332,1.067994 \H,-3.271504067,0.6000086349,-0.111938\H,-3.2985628781,-1.0922373681,- 0.605643\H,-1.0065661955,1.7521268877,0.11872\H,-0.4177160784,0.702551 9534,1.381475\H,1.4058288033,1.7620901569,0.080983\H,0.8381948934,0.95 54000935,-1.386395\H,-0.8377028671,-1.1910850935,-0.632006\Version=IA 64L-G03RevC.02\State=2-A\HF=-617.3770399\S2=0.75582\S2-1=0.\S2A=0.7500 24\RMSD=9.072e-09\RMSF=3.121e-06\Dipole=-0.6235206,0.6253765,-0.046305 3\PG=C01 [X(C4H8Cl1)]\@

TS: Intermolecular β-Hydrogen Elimination from CH₃CH•CH₂CH₂Cl (11)

1\1\GINC-AC13\FTS\UmPWPW91\6-31+G(d,p)\C6H11Cl2(2)\EXK501\29-Nov-2005\ 0\0\# MPWPW91/6-31+G** OPT=(TS,CALCF,NOEIGENTEST,MAXCYC=300) FREQ=NORA MAN IOP(3/76=0572004280) MAXDISK=134217728\ts_CH3CHCH2CH2Cl_BHelim-n\ 0,2\C1,-2.9250490937,-1.3035534425,-0.5877246951\C,-1.2545500125,-0.9 924403323,-0.0088578449\C,-1.0095840144,0.4603159376,0.2663207591\C,-0 .7525380507,1.3237115996,-0.8044597856\C,-0.8412439411,2.8018224984,-0 .7104921181\H,-1.4852143663,3.204492793,-1.4943400597\H,-1.244660624,3 .1198361329,0.2485173784\H,0.1342774731,3.2757621619,-0.8403864614\H,0 .1601609267,0.3550950547,0.9651678117\H,-1.6250637511,0.8672960503,1.0 657991525\H,-1.1357183789,-1.5975336684,0.8834375379\H,-0.586008297,-1 .3647938048,-0.7782980842\H,-0.3804796794,0.9010646974,-1.7297103364\C ,1.3098095866,0.1700644077,1.7352371892\C,2.4022493955,0.4275850072,0. 9235103392\C1,3.0406940754,-0.7770999488,-0.1202718409\H,2.8187157588, 1.4075494743,0.7638862394\H,1.1403603676,-0.8552712185,2.0430114542\H, 1.1128081019,0.9112552709,2.5013052462\Version=IA64L-G03RevC.02\State =2-A\HF=-1155.5111318\S2=0.898172\S2-1=0.\S2A=0.753395\RMSD=8.119e-09\ RMSF=4.034e-06\Dipole=0.3602103,0.8476948,0.5122709\PG=C01 [X(C6H11Cl2)]\@

CH₂ClCH=CHCH₃

```
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)]\@
```

CH₃CHCl•

```
1\1\GINC-AC10\FOpt\UmPWPW91\6-31+G(d,p)\C2H4Cl1(2)\EXK501\17-Oct-2006\
0\# MPWPW91/6-31+G** OPT IOP(3/76=0572004280) MAXDISK=134217728\MeCH
Cl_rad_MPW1K\0,2\C,0.4417011225,0.5947727855,-0.0626012545\C,1.640746
569,-0.2633221608,0.0040763923\H,1.7636189013,-0.7191807787,0.99089406
53\H,2.5292315343,0.3287702118,-0.2034018942\H,1.5882700485,-1.0735759
143,-0.7218803103\Cl,-1.1074384907,-0.128015072,0.0083859531\H,0.45064
77088,1.6515389571,0.1429761085\Version=IA64L-G03RevC.02\State=2-A\HF
=-538.7593197\S2=0.756232\S2-1=0.\S2A=0.750029\RMSD=9.411e-09\RMSF=1.4
06e-05\Dipole=0.6576736,0.1578777,0.0906724\PG=C01 [X(C2H4Cl1)]\@
```

TS: H-abstraction from a chloroallylic end group (12)

```
1\1\GINC-AC57\FTS\UmPWPW91\6-31+G(d,p)\C8H14Cl3(2)\MLC501\17-Aug-2007\
0\# MPWPW91/6-31+G** IOP(3/76=0572004280) OPT=(TS,calcf, noeigentest,
maxcyc=200) INT(grid=ultrafine) maxdisk=671088640\H-abs_CAEG-geom\0,
2\C,0.3491998972,-0.7669999983,-0.1028044977\C,1.5975571085,-0.0852868
687,0.218054014\C,1.8309560456,1.1961298862,-0.0799712801\C,3.05634120
63,1.9476108683,0.3035255952\H,2.3367984964,-0.6555435953,0.767755915\
H,1.0800916776,1.7441538338,-0.6384809669\Cl,0.5269411762,-2.469806344
4,-0.5323220933\H,-0.4073409145,-0.7911605801,0.9339692644\H,-0.269133
8187,-0.2676983086,-0.8409639085\H,3.5596171854,2.346560027,-0.5772257
642\H,2.8074863002,2.8001672355,0.9361936126\H,3.7602538995,1.31796687
19,0.8423893932\C,-1.2515780385,-0.8290488301,2.0524602423\Cl,-1.90100
53697,0.7896672729,2.1873935972\H,-2.0295047284,-1.5228602551,1.758703
3034\C,-0.375235755,-1.254309019,3.1857101265\C,-1.0698626376,-1.40114
69021,4.5309430418\H,0.4287451909,-0.5263490649,3.3097440941\H,0.08308
78696,-2.2073362737,2.9165652648\C,-0.1048210613,-1.7393121124,5.64220
19145\H,-1.6143215673,-0.4899776699,4.7632885248\Cl,-2.3329865187,-2.6
791257622,4.4268021728\H,-0.6258282475,-1.8506991215,6.5888585392\H,0.
423306005,-2.6664215595,5.42987208\H,0.6272465988,-0.9391537297,5.7454
178149\Version=IA64L-G03RevD.01\State=2-A\HF=-1693.766906\S2=0.777357
\S2-1=0.\S2A=0.750452\RMSD=4.410e-09\RMSF=1.198e-06\Thermal=0.\Dipole=
1.041486,0.8992798,0.2838987\PG=C01 [X(C8H14Cl3)]\@
```

•CHClCH=CH-CH₃

```
1\1\GINC-AC14\FOpt\UmPWPW91\6-31+G(d,p)\C4H6Cl1(2)\MLC501\17-Aug-2007\
0\# MPWPW91/6-31+G** IOP(3/76=0572004280) OPT INT(grid=ultrafine) max
disk=671088640\allylic_rad-geom2\0,2\C,-0.0106241551,-0.0028669632,-
0.0013829667\C,1.3685759288,0.049097126,0.0010773977\C,2.1598613405,1.
1752788011,-0.0016004566\C,3.6446819338,1.1414610609,0.0014136385\H,4.
051970948,1.651228027,-0.8732061317\Cl,-1.0023280445,1.3960716557,-0.0
090925547\H,4.0485113221,1.6556016,0.8750989866\H,4.0259794587,0.12274
97503,0.004741969\H,1.8548076502,-0.9196139451,0.0056669068\H,1.680330
0147,2.1447326846,-0.0060476988\H,-0.5621663972,-0.9266097974,0.002210
91\Version=IA64L-G03RevD.01\State=2-A\HF=-616.1608651\S2=0.809516\S2-
1=0.\S2A=0.750646\RMSD=7.075e-09\RMSF=2.020e-05\Thermal=0.\Dipole=0.61
19455,-0.3389457,0.0030296\PG=C01 [X(C4H6Cl1)]\@
```

CH₃CHClCH₂CH₂Cl

```
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-alb3-mpwlk\0,1\C1\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\C1,4,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\RMSE=4.765e-09\RMSF=6.24
0e-05\Dipole=0.4802076,0.7098528,0.5058297\PG=C01 [X(C4H8Cl2)]\\@
```

Normal Propagation TS (13)

```
1\1\GINC-LC57\FTS\UmPWPW91\6-31+G(d,p)\C6H10Cl3(2)\MLC501\19-Apr-2004\
0\\# MPWPW91/6-31+G** OPT=(TS,CALCF,NOEIGENTEST,MAXCYC=300) IOP(3/76=
0572004280) MAXDISK=268435456\\TS_prop-clb-mpwlk\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\C1,3.1953140587,-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\C1,-0.6522197582,1.8939425375,1.6590116266\H,0.16
35098198,-0.6761490061,-0.8140736418\H,0.2479366674,1.0717035217,-0.97
03353015\C1,-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\RMSE=3.733e-09\RMSF=2.872e-06\Dipol
e=0.247431,0.1867976,-0.1426937\PG=C01 [X(C6H10Cl3)]\\@
```

Head-to-Head Propagation TS (14)

```
1\1\GINC-LC21\FTS\UmPWPW91\6-31+G(d,p)\C6H10Cl3(2)\EXK501\31-Oct-2006\
0\\# MPWPW91/6-31+G** OPT=(TS,CALCF,NOEIGENTEST,MAXCYC=200) IOP(3/76=
0572004280) MAXDISK=268435456\\ts_HHaddn_d2_a2\0,2\C,0.9477460811,-1.
9100123578,2.4857276371\H,0.9310987443,-1.9072337176,3.5718750795\H,1.
9848168204,-1.8860031384,2.1580157855\H,0.4956274777,-2.8380515536,2.1
37652516\C,0.1795999095,-0.7340909894,1.9310551783\C1,0.8726303935,0.7
938361748,2.583307302\H,-0.8468719863,-0.748085054,2.2874957089\C,0.19
63800763,-0.6999081541,0.409235142\H,1.2262169194,-0.5922600817,0.0668
940333\H,-0.1721360372,-1.6641718954,0.0550503925\C,-0.6099045659,0.38
36942049,-0.208106591\C1,-2.3285466674,0.2518059634,-0.0290302551\H,-0
.2720516084,1.4050631673,-0.1118351279\C,-0.2350550671,0.2356783659,-2
.4204414762\H,-1.0001205807,0.990095439,-2.5085769593\C1,1.3728020394,
0.9001494589,-2.4646746036\C,-0.4503441607,-1.0540060191,-2.7701371972
\H,-1.4645380715,-1.41025444,-2.8611230966\H,0.3603666689,-1.755686179
,-2.8826860267\\Version=IA32L-G03RevC.02\State=2-A\HF=-1615.1484242\S2
=0.821796\S2-1=0.\S2A=0.750775\RMSE=9.434e-09\RMSF=5.099e-06\Dipole=-0
.2166851,-1.0120392,-0.1918649\PG=C01 [X(C6H10Cl3)]\\@
```

CH₃CHClCHClCH₂•

```
1\1\GINC-AC6\FOpt\UmPWPW91\6-31+G(d,p)\C4H7Cl2(2)\EXK501\21-Nov-2006\0
\\# MPWPW91/6-31+G** OPT IOP(3/76=0572004280) MAXDISK=134217728\\propa
fterHH_SM_alb2\0,2\C,0.6606108403,-1.2797714678,1.2847148877\H,0.6953
768468,-1.2438739113,2.3695597307\H,1.6776658794,-1.3827483602,0.91257
82711\H,0.0875649793,-2.1523923297,0.9839016282\C,0.0185214164,-0.0252
124791,0.7444812497\C1,0.9307615791,1.4037825019,1.3470210183\H,-0.991
7502209,0.09100957,1.1289782892\C,-0.0128159408,0.0748226787,-0.773625
6513\C1,-0.9857827409,-1.350156605,-1.4023585413\H,0.9829368857,-0.087
6700369,-1.1766996166\C,-0.617378365,1.3045390915,-1.2938753672\H,-1.4
16671729,1.7853814729,-0.7527753868\H,-0.3933905962,1.632386409,-2.294
9757398\\Version=IA64L-G03RevC.02\State=2-A\HF=-1076.9785047\S2=0.7568
84\S2-1=0.\S2A=0.750034\RMSE=3.231e-09\RMSF=7.206e-06\Dipole=0.0139098
,-0.0313979,0.0310875\PG=C01 [X(C4H7Cl2)]\\@
```

TS: Head-to-Tail Propagation by Head-to-Head Adduct Radical (15)

1\1\GINC-AC2\FTS\UmpPWPW91\6-31+G(d,p)\C6H10Cl3(2)\EXK501\15-Nov-2006\0
\\# MPWPW91/6-31+G** OPT=(TS,CALCFC,NOEIGENTEST,MAXCYC=200) IOP(3/76=0
572004280) MAXDISK=134217728\\ts_propafterHH_d2_a1\\0,2\C,0.5164419576
,-1.6395574414,2.592718478\H,0.5051700485,-1.6007832152,3.6780920916\H
,1.5442362676,-1.5216570414,2.2562300407\H,0.1535736113,-2.6133765868,
2.2764851524\C,-0.3595943399,-0.5465330961,2.0272092153\C1,0.206227398
2,1.0339140787,2.6741860066\H,-1.3852969561,-0.6510454553,2.3706925576
\C,-0.3501425409,-0.4514121019,0.4982589918\C1,-0.9535209821,-2.028787
6257,-0.1411420382\H,0.6811124843,-0.3696548167,0.1593773744\C,-1.1696
257496,0.648233178,-0.064435395\H,-0.7731942746,1.646019389,0.03924032
58\H,-2.2446508159,0.5395211929,-0.0447207322\C,-0.8748711822,0.576019
1547,-2.3901874095\H,-1.5631589736,-0.2525391207,-2.4439847\H,-1.27771
81823,1.5756820213,-2.426883403\C,0.4249733769,0.3412223559,-2.6398767
578\H,0.8470061379,-0.6459365102,-2.7316382454\C1,1.5937542617,1.60228
16557,-2.7256918036\\Version=IA64L-G03RevC.02\State=2-A\HF=-1615.14599
22\S2=0.809956\S2-1=0.\S2A=0.750629\RMSD=9.134e-09\RMSF=5.463e-06\Dipo
le=-0.4644778,-0.4135626,0.1336464\PG=C01 [X(C6H10Cl3)]\\@

CH₃CHClCH•CH₂Cl

1\1\GINC-AC40\FOpt\UmpPWPW91\6-31+G(d,p)\C4H7Cl2(2)\EXK501\30-Nov-2005\
0\\# MPWPW91/6-31+G** OPT IOP(3/76=0572004280) MAXDISK=134217728\\PVCd
im+HTH-12Clprod\\0,2\H,-0.8067497632,-0.4515044032,0.9482700637\C,-0.9
863604041,0.0640272091,0.007878641\C1,-1.2915134029,1.7961400545,0.528
658095\C,-2.221523049,-0.4696663248,-0.6733391696\C,0.2222218593,0.040
0334846,-0.8321641968\C,1.563382355,0.0529496349,-0.2365862478\H,1.609
2966737,0.6698481293,0.6556435923\H,2.3264446991,0.3675078905,-0.93771
19739\C1,2.0487632798,-1.6131280574,0.3056016787\H,0.1135577287,0.0082
373387,-1.9063064544\H,-2.4290756888,0.08378115,-1.5862776431\H,-2.065
540384,-1.5167994554,-0.9285400678\H,-3.0875057399,-0.3963386237,-0.02
22278295\\Version=IA64L-G03RevC.02\State=2-A\HF=-1076.9844159\S2=0.757
949\S2-1=0.\S2A=0.75005\RMSD=8.652e-09\RMSF=1.213e-05\Dipole=-0.192474
3,-0.0985156,-0.5628661\PG=C01 [X(C4H7Cl2)]\\@

TS: Propagation by Mid-Chain Radical (16)

1\1\GINC-AC46\FTS\UmpPWPW91\6-31+G(d,p)\C6H10Cl3(2)\EXK501\02-Dec-2005\
0\\# MPWPW91/6-31+G** OPT=(TS,CALCFC,NOEIGENTEST,MAXCYC=300) IOP(3/76=
0572004280) MAXDISK=134217728\\ts_PVCdim+HTH-12Clprod-prop-e\\0,2\H,-2
.3993379449,-0.0234202964,0.8793302959\C,-1.574172057,-0.6849047839,0.
6101997569\C1,-2.0831850076,-1.3435215502,-0.9981118465\C,-1.480961648
2,-1.813415454,1.610582606\C,-0.3334802033,0.1333123464,0.4917188753\C
, -0.3060241154,1.285607561,-0.4302495908\H,-0.6693421169,1.0296301056,
-1.4195093358\H,0.6851368527,1.7169041567,-0.4988023505\C1,-1.38213540
41,2.6185882938,0.1609648986\H,0.1847988516,0.2800094893,1.4314425238\
H,-0.7323339536,-2.5445465934,1.317718321\H,-1.2122497691,-1.410123356
7,2.586014059\H,-2.4351015017,-2.3236204285,1.7028600553\C,1.327697344
5,-1.2287716102,-0.3650844441\C,2.347031436,-0.464590517,-0.8092216306
\H,0.6383108545,-1.6386529636,-1.0872621908\H,1.3872577784,-1.70256171
18,0.6017226393\C1,3.5978037656,0.0977919864,0.2285662959\H,2.42009939
25,-0.0856420652,-1.8153163689\\Version=IA64L-G03RevC.02\State=2-A\HF=
-1615.1507189\S2=0.813919\S2-1=0.\S2A=0.750765\RMSD=7.816e-09\RMSF=3.0
52e-06\Dipole=0.2196736,-0.6391124,0.2935406\PG=C01 [X(C6H10Cl3)]\\@

TS: Propagation of Allylic Radical (17)

1\1\GINC-AC31\FTS\UmpPWPW91\6-31+G(d,p)\C6H9Cl2(2)\MLC501\17-Aug-2007\0
\\# MPWPW91/6-31+G** IOP(3/76=0572004280) OPT=(TS,calcfc,noeigentest,m
axcyc=200) INT(grid=ultrafine) maxdisk=671088640\\allylic_prop_TS2-geo
m\\0,2\C,0.0099267057,-0.0187196511,-0.090685324\C,1.3684889166,0.0121
568197,-0.0246866052\C,2.018155168,2.0719820783,0.1051866237\C,3.44126
32271,1.9857798306,0.0391756641\C,4.3111257126,2.0578306428,1.06641212
47\C,5.7843882192,1.9117089492,0.9263866419\H,6.3001304287,2.810317824
7,1.2666382956\H,-0.6344142692,0.0108698934,0.7713648302\C1,-0.8259218
173,0.1365102563,-1.5857694275\H,1.8302181127,-0.2256835944,0.92197531
19\H,1.9504403261,-0.1805871204,-0.9131315673\C1,1.2753414747,2.661421
1314,1.5584585291\H,6.1556695504,1.089285097,1.5391521906\H,6.07565599
7,1.7240973309,-0.1045567435\H,3.8258190683,1.7965861169,-0.9572700127
\H,3.9268561514,2.2535980596,2.0593123692\H,1.4754070282,2.3850763352,
-0.7725829009\\Version=IA64L-G03RevD.01\State=2-A\HF=-1154.3177689\S2=
0.855544\S2-1=0.\S2A=0.756033\RMSD=9.970e-09\RMSF=1.454e-06\Thermal=0.
\Dipole=0.9444735,-0.1572109,0.0904893\PG=C01 [X(C6H9Cl2)]\\@

CH₂ClCH=CHCHClCH₂CHCl•

1\1\GINC-AC32\FOpt\UmPWPW91\6-31+G(d,p)\C6H9Cl2(2)\MLC501\22-Aug-2007\0\\# MPWPW91/6-31+G** IOP(3/76=0572004280) OPT INT(grid=ultrafine) max disk=671088640\\allylic_prop_prod-geom\\0,2\C,-0.2449993108,-0.0481948493,-0.096511547\C,1.2318952528,-0.07521265,-0.031552009\C,1.898347088,1.3010774521,0.0802551621\C,3.382881337,1.1952111718,-0.0462654884\C,4.3049262556,1.5408482655,0.8409809429\C,5.7724952168,1.3946147119,0.6301880422\H,6.2711709019,2.3612543983,0.6998175539\H,-0.877667594,-0.0671428217,0.7738884573\C1,-1.0003827643,0.5277858936,-1.5188283292\H,1.5387286889,-0.678549391,0.8218845781\H,1.6281445296,-0.5523809158,-0.9302684125\C1,1.3771594353,2.090867199,1.6011994895\H,6.2124409641,0.7581282456,1.3978431395\H,6.000954154,0.9632395807,-0.3416365879\H,3.6945652497,0.7760317566,-0.9980634598\H,3.9875520977,1.965049638,1.7849222844\H,1.5120784975,1.9417323149,-0.7109938161\\Version=IA64L-G03RevD.01\State=2-A\HF=-1154.3610333\S2=0.756297\S2-1=0.\S2A=0.750029\RMSD=8.561e-09\RMSF=3.316e-05\Thermal=0.\Dipole=0.7811487,-0.4191168,-0.0911513\PG=C01 [X(C6H9Cl2)]\\@

Figure S1. Development of the monomer weight fraction in the polymer-rich phase with the course of the polymerization.

APPENDIX I

Calculations of the numbers of defect structures from NMR spectra

The numbers of different defect structures per 1000 vinyl chloride units were calculated from the areas of their signals in proton NMR according to the formulae below. The area of the CHCl peak was set to 1000 and the areas of the protons contained in the defects were then measured.

	Per 1000 VC units ($A_{\text{CHCl}} = 1000$)	Per chain
All unsaturated protons	$N_u = \frac{A_u}{2 * (A_{\text{CHCl}})} * 10^3$	$N_u' = \frac{N_u}{10^3} * \overline{\text{DPn}}$
Chloroallylic end groups	$N_{\text{CIA}} = \frac{A_{\text{CIA}}}{2 * (A_{\text{CHCl}})} * 10^3$	$N_{\text{CIA}}' = \frac{N_{\text{CIA}}}{10^3} * \overline{\text{DPn}}$
Internal double bonds	$N_i = N_u - N_{\text{CIA}}$	$N_i' = N_u' - N_{\text{CIA}}'$
Saturated chloromethyl end groups	$N_s = \frac{A_s}{2 * (A_{\text{CHCl}})} * 10^3$	$N_s' = \frac{N_s}{10^3} * \overline{\text{DPn}}$
Initiator end groups	$N_{\text{ini}} = \frac{A_{\text{ini}}}{2 * (A_{\text{CHCl}})} * 10^3$	$N_{\text{ini}}' = \frac{N_{\text{ini}}}{10^3} * \overline{\text{DPn}}$
Branches	$N_b = \frac{N_b'}{\overline{\text{DPn}}} * 10^3$	$N_b' = (N_s' + N_i' + N_{\text{ini}}) - 2$

APPENDIX II

Diffusion controlled reaction rate coefficients

Apparent rate coefficients of the reactions taking place in heterogeneous media are usually composed from the terms k_{chem} (rate coefficient corresponding to chemically controlled reaction) and k_{diff} (diffusion contribution), having the following relationship:¹

$$\frac{1}{k_{obs}} = \frac{1}{k_{chem}} + \frac{1}{k_{diff}} \quad (1)$$

The diffusion contributions to the rate coefficients for the reactions taking place in our system were calculated using the model developed by De Roo *et al.*²

The diffusion contribution

k_{diff} can be calculated using the Smoluchowski model.³

$$k_{diff,2} = 4\pi(r_y + r_z)(D_y + D_z)N_A \quad (2)$$

$(r_y + r_z)$ distance between the two species when reaction occurs

$(D_y + D_z)$ mutual diffusion coefficient consisting of two contributions of the reacting species y and z

N_A Avogadro constant

$(r_y + r_z)$ was taken as the Lennard-Jones diameter of a monomer molecule

$$\sigma_m^4 = 4.69 \times 10^{-10} \text{ m}$$

The general expression was used for the calculation of the diffusion contributions of the rate coefficients of the propagation and chain transfer to polymer in the following form:

$$\text{propagation} \quad k_{diff,2} = 4\pi\sigma_m D_m N_A \quad (3)$$

$$\text{transfer to polymer} \quad k_{diff,2} = 4\pi\sigma_m D_p N_A \quad (4)$$

D_m self-diffusion coefficient of monomer

D_p self-diffusion coefficient + reaction diffusion coefficient of polymer

Self-diffusion coefficients

These coefficients are calculated using free volume theory,⁵

$$D_m = D_{m,0} \exp\left(\frac{-E^*}{RT}\right) \exp\left(\frac{-\tilde{V}_{mj}^*}{\tilde{V}_{FH} / \gamma}\right) \quad (5)$$

$$D_p = D_{p,0} \exp\left(\frac{-\tilde{V}_{pj}^*}{\tilde{V}_{FH} / \gamma}\right) \quad (6)$$

where

$$\tilde{V}_{xj}^* = \hat{V}_x^* M_{xj} \quad (7)$$

$D_{x,0}$ pre-exponential factor

E^* activation energy needed to make a diffusional jump

$\left(\frac{-\tilde{V}_{xj}^*}{\tilde{V}_{FH} / \gamma}\right)$ free volume contribution

$\hat{V}_x^*$ specific volume a molecule needs to make a diffusional jump

$\tilde{V}_{FH}$ hole free volume of the polymer-monomer mixture of the polymer-rich phase available for diffusion

γ overlap factor

$$\tilde{V}_{FH} / \gamma = \frac{\hat{V}_{FH} / \gamma}{\frac{w_m}{M_{mj}} + \frac{w_p}{M_{pj}}} \quad (8)$$

$\hat{V}_{FH}$ specific hole free volume

w_x monomer or polymer weight fraction in the polymer rich phase

M_{xj} molecular mass of the monomer or macroradical jumping unit

$$\hat{V}_{FH} / \gamma = w_m \frac{\hat{V}_m^0(T_{g,m})}{\gamma_m} (f_{H,m}^G + \alpha_m (T - T_{g,m})) + w_p \frac{\hat{V}_p^0(T_{g,p})}{\gamma_p} (f_{H,p}^G - (\alpha_p - \alpha_{c,p})(T_{g,p} - T)) \quad (9)$$

α_x monomer; polymer thermal expansion coefficient

$T_{g,x}$ glass transition temperature of the pure monomer or polymer

$f_{H,x}^G$ fractional hole free volume of the pure component at T_g

γ_x hole free volume overlap factor

$$\hat{V}_x^0(T_{g,x}) = 1 / \rho_x(T_{g,x}) \quad (10)$$

$$\rho_m = 94.469 / 0.2707^{1+(1-T/432)^{0.2716}} \quad (11)$$

$$\rho_p = 10^3 \exp(0.4296 - 3.274 \times 10^{-4} T) \quad (12)$$

$\hat{V}_x^0(T_{g,x})$ specific volume of the pure component at T_g

ρ_x density of the monomer or polymer

$$\alpha_{c,p} = \frac{1}{T_{g,p}} \ln \left(\frac{\hat{V}_p^0(T_{g,p})(1 - f_{H,p}^G)}{\hat{V}_p^0(0)} \right) \quad (13)$$

$\alpha_{c,p}$ Close-packed crystalline state expansion coefficient⁶

$\hat{V}_x^0(0)$ specific volume of the pure component at 0K

x = m,p

Pre-exponential factors

Monomer

$D_{m,0}$ is calculated from the Dullien equation:⁷

$$D_{m,0} = \frac{0.124 \times 10^{-16} \tilde{V}_{c,m}^{2/3} RT}{M_m \eta \hat{V}_m^0} \exp \left(\frac{\gamma_m \hat{V}_m^* / K_{11}}{K_{21} - T_{g,m} + T} \right) \quad (14)$$

$\tilde{V}_{c,m}$ Monomer critical volume

M_m Monomer molecular mass

η Pure monomer viscosity

$\hat{V}_m^0$ Pure monomer volume

K_{11} / γ_m Monomer free volume parameters

K_{21}

$$K_{11} / \gamma_m = \hat{V}_m^0(T_{g,m}) \alpha_m / \gamma_m \quad (15)$$

$$K_{21} = f_{H,x}^G / \alpha_m \quad (16)$$

Property	Units	Monomer	Polymer
$\rho_x = 1/\hat{V}_x^0$ ^{9,17}	[g l ⁻¹]	842.93	1379.04
η	[N m ⁻² s]	$6.4 \times 10^{-9} T^2 - 5.27 \times 10^{-6} T + 1.18 \times 10^{-3}$	—
$\hat{V}_x^* = \hat{V}_x^0(0)$ ⁸	[m ³ kg ⁻¹]	7.94×10^{-4}	6.66×10^{-4}
$\hat{V}_{xj}^* = \hat{V}_x^*(0)$ ⁸	[m ³ mol ⁻¹]	49.6×10^{-6}	132.85×10^{-6}
$f_{H,x}^G$ ⁵	[-]	0.025	0.025
α_x ^{9,10}	[K ⁻¹]	1.42×10^{-3}	5.85×10^{-4}
$T_{g,x}$	[K]	70	353.15
γ_x	[-]	1.0	1.0
E^*	[kJ mol ⁻¹]	16.4	-
M_m	[kg mol ⁻¹]	0.0625	-

Polymer

$D_{p,0}$ is determined by calculating the polymer diffusion coefficient k_{diff} at $w_p=1$, and setting this coefficient equal to the diffusion coefficient derived from the reptation theory.^{11,12}

$$D_{reptation} = \frac{G_N^0}{135} \left(\frac{\rho_p RT}{G_N^0} \right)^2 \frac{\langle R^2 \rangle}{M} \frac{M_{cr}}{M^2 \eta_{cr}} \quad (17)$$

G_N^0 Shear modulus of the rubbery plateau
 $\langle R^2 \rangle$ Mean-square end-to-end distance of the polymer chain with molecular mass M
 ρ_p Polymer density
 η_{cr} Zero shear melt viscosity at the M_{cr}
 M_{cr} Critical molecular mass of the polymer

$$D_{reptation} \Big|_{w_p=1; T=1.2T_{g,p}} = D_p \Big|_{w_p=1; T=1.2T_{g,p}} \quad (18)$$

$$\downarrow$$

$$D_{p,0} = \frac{6.53 \times 10^{-10}}{M^{1.892}} \quad (19)$$

Property		Units	Value/Expression
$G_N^0 = 2\rho_p RT / M_{cr}$	12	[N m ⁻²]	1.5 x 10 ⁶
$\langle R^2 \rangle^{1/2}$	2	[m]	2.833 x 10 ⁻⁹ M ^{0.554}
$\log \eta_{cr} (1.2T_{g,p})$	8	[N m ⁻² s]	3.89
M_{cr}	8	[kg mol ⁻¹]	6.25

Activation energy

E^* is estimated from the fit of its graph^{6,13} vs. $(\delta_m - \delta_p)^2 \tilde{V}_m^0$

$$\log(E^*) = 0.8988 \ln(\log((\delta_m - \delta_p)^2 \tilde{V}_m^0 / 4.1868)) + 3.4575 \quad (20)$$

$\tilde{V}_m^0$ Molar volume of the pure monomer at a reference temperature 20°C

δ_x Solubility parameters

$$\delta_m = (E_{coh} / \tilde{V}_m^0)^{1/2} \quad (21)$$

$$E_{coh} = \Delta H_{vap} - RT \quad (22)$$

Property	Units	Monomer	Polymer
ΔH_{vap}	[kJ mol ⁻¹]	20.4	-
δ_x	⁸ [(Jm ⁻³) ^{1/2}]	16.19 x 10 ³	16.73 x 10 ³

Free volume parameters

$\tilde{V}_{xj}^*$ are calculated as the size of the jump unit at 0K.⁶

$\tilde{V}_{mj}^*$ is the volume of the molecule itself.

The equation for the calculation of the $\tilde{V}_{pj}^*$ was obtained by fitting of the tabulated values for some common polymers.⁶

$$\tilde{V}_{pj}^* = 0.6224 \times 10^{-6} T_{g,p} - 86.95 \times 10^{-6} \quad (23)$$

γ_m and γ_p were set to their highest theoretical value 1.

Reaction diffusion coefficient

The so-called reaction diffusion coefficient expresses the segmental motion of the radical chain end due to the propagation⁴.

$$D_p(rd) = \frac{1}{6} k_{p,obs} [M_p] a^2 \quad (24)$$

$k_{p,obs}$ Apparent propagation rate coefficient

$[M_p]$ Molar concentration of the monomer in the polymer rich phase

a Root-mean-square end-to-end distance per square root of the number of monomer units in a polymer chain ($=6.09 \times 10^{-10}$ m)

Distribution of the monomer and polymer during the suspension polymerization of vinyl chloride

The amounts of monomer and/or polymer in either monomer or polymer-rich phase were calculated using the model developed by Xie *et al.*¹⁴

$$w_p = \frac{m_{p,X}}{m_{m,0} - m_{m,g,X} - m_{m,aq,X}} \quad (25)$$

w_p weight fraction of polymer in polymer rich phase at conversion X

$m_{p,X}$ mass of polymer formed at $X=X$ $m_{m,0}$

$m_{m,0}$ mass of VCM initially charged

$m_{m,g,X}$ mass of VCM in gaseous phase at X

$m_{m,aq,X}$ mass of VCM in aqueous phase at X

A very important parameter in the description of the distribution of the monomer is critical conversion X_f . At this point, the monomer as a separate phase is consumed and the pressure in the reactor begins to drop. The X_f in our system was determined to occur at 60%.¹⁵

$X < X_f$

The amount of the monomer in the gaseous and aqueous phase does not contribute to the polymerization at conversions $X < X_f$. The composition of the polymer rich phase remains constant ($w_p=0.66$), because monomer is being replaced from the pure liquid monomer phase.

$$m_{m,g,X < X_f} = \frac{M_m P_{m,0}}{RT} \left[(1 - v_{r,0}) V_r + \frac{X m_{m,0} (1/\rho_m - 1/\rho_p)}{1 - P_{m,0} M_m / (RT \rho_m)} \right] \quad (26)$$

$$m_{m,aq,X < X_f} = K m_w \quad (27)$$

$X > X_f$

At conversion $> X_f$ the pure liquid monomer phase is depleted and the polymerization goes on in the pure polymer-rich phase. The monomer necessary for the propagation is being taken from gas and aqueous phase.

$$m_{m,g,X > X_f} = \frac{M_m P_m}{RT} \left[(1 - v_{r,0}) V_r + \frac{X_f m_{m,0} (1/\rho_m - 1/\rho_p)}{1 - \rho_{g,0} / \rho_p} + (X - X_f) m_{m,0} (1/\rho_m - 1/\rho_p) \right] \quad (28)$$

$$m_{m,aq,X > X_f} = K m_w P_m / P_{m,0} \quad (29)$$

$$\rho_{g,0} = P_{m,0} M_m / (RT) \quad (30)$$

$$v_{r,0} = (m_w / \rho_w + m_{m,0} / \rho_m - \rho_{g,0} V_r / \rho_m) / (V_r (1 - \rho_{g,0} / \rho_m)) \quad (31)$$

	Property	Units	Value/Expression
P_m	pressure in the reactor	[bar]	
$P_{m,0}$	vapor pressure of monomer	[bar]	$P_{m,0} = 12722 \exp(-2411.7/T)$
R	universal gas constant	[bar l mol ⁻¹ K ⁻¹]	8.314×10^{-2}
T	temperature	[K]	330.5
X	monomer conversion	[-]	
X_f	critical monomer conversion	[-]	
K	solubility constant ¹⁶	[-]	1.21×10^{-2}
V_r	volume of the reactor	[l]	1.077
m_w	mass water charged	[g]	349.29
$m_{m,0}$	mass monomer initially charged	[g]	175
$v_{r,0}$	initial degree of charging of the reactor	[-]	0.5063
$\rho_{g,0}$	vapor density at the vapor pressure of the monomer	[g l ⁻¹]	19.85
ρ_w	water density ¹⁷	[g l ⁻¹]	$\rho_w = 1011 - 0.4484t = 1002.03$
t	temperature	[°C]	

References:

1. See for example: Hamielec, A.E. In *Science and Technology of Polymer Colloids*; Poehlein, G.W., Ottweil, R.H., Goodwin, J.W.E., Eds.; Martinus Nijhof Publishers: The Hague, Denmark, 1983; p140.
2. De Roo, T.; Heynderickx, G. J.; Marin, G. B. *Macromol.Symp.* **2004**, 206, 215-228.
3. Smoluchowski, M.Z. *Phys. Chem.* **1918**, 92, 129.

4. Clay, P. A.; Gilbert, R. G. *Macromolecules* **1995**, 28, 552-569.
5. Bueche, F. *Physical Properties of Polymers*; Wiley- Interscience: New York, 1962.
6. See for example: Vrentas, J. S.; Vrentas, C. M. *Eur. Polym. J.* **1998**, 34, 797-803.
7. See for example: Zielinski, J. M. *Macromolecules* **1996**, 29, 6044-6047; Dullien, A.L. *AIChE J.* **1972**, 18(1), 62-70.
8. Van Krevelen, D.W. *Properties of Polymers*, 3rd ed.; Elsevier: Amsterdam, 1997.
9. Perry, R.H; Green, D.W. *Perry's Chemical Engineers' Handbook*, 7th ed.; McGraw-Hill: New York, 1998.
10. Bandrup, J.; Immergut, E.H. *Handbook of Polymers*, 3rd ed.; Wiley: New York, 1989.
11. Masaro, L.; Zhu, X. X. *Prog. Polym. Sci.* **1999**, 24, 731-775.
12. Graessley, W.W. *J. Polym. Sci., Polym. Phys. Ed.*, **1980**, 18, 27-34.
13. Tonge, M. P.; Gilbert, R. G. *Polymer* **2001**, 42, 1393-1405.
14. Xie, T. Y.; Hamielec, A. E.; Wood, P. E.; Woods, D. R. *J. Appl. Polym. Sci.* **1987**, 34, 1749-1766.
15. Pauwels, K.F.D. *New aspects of the suspension polymerization of vinyl chloride in relation to the low thermal stability of poly(vinyl chloride)*, Dissertation: Groningen University, 2004.
<http://dissertations.ub.rug.nl/faculties/science/2004/k.f.d.pauwels/>
16. Weast, R.C. *Handbook of Chemistry and physics*; The Chemical Rubber Co.: Ohio, 1970
17. Xie, T. Y.; Hamielec, A. E.; Wood, P. E.; Woods, D. R. *Polymer* **1991**, 32, 537-557.

APPENDIX III

Calculation of reaction rates and probabilities of the formation of internal unsaturations by different side reactions

1–6 backbiting followed by β -elimination:

$$P_{u1-6} = P_{1-6} \times P_{\beta\text{-elim.}} \quad (32)$$

$$P_{1-6} = (v_{fwd1-6} \cdot v_{rev1-6}) / ((v_{fwd1-6} \cdot v_{rev1-6}) + (v_{fwd1-5} \cdot v_{rev1-5}) + (v_{fwd1-2} \cdot v_{rev1-2}) + (v_{fwd \text{ tr inter}} \cdot v_{rev \text{ tr inter}}) + (v_{fwd \text{ HH}} \cdot v_{rev \text{ HH}}) + v_p + v_t) = (k_{fwd1-6} \cdot k_{rev1-6}) / ((k_{fwd1-6} \cdot k_{rev1-6}) + (k_{fwd1-5} \cdot k_{rev1-5}) + (k_{fwd1-2} \cdot k_{rev1-2}) + (k_{fwd \text{ tr inter}} \cdot k_{rev \text{ tr inter}}) + (k_{fwd \text{ HH}} \cdot k_{rev \text{ HH}}) + k_p + k_t) [P] + (k_{fwd \text{ HH}} [M] + k_p [M] + k_t [P \cdot]) \quad (33)$$

$$P_{\beta\text{-elim.}} = (v_{fwd \beta\text{-elim.}} \cdot v_{rev \beta\text{-elim.}}) / (v_p \cdot 1-6 + (v_{fwd \beta\text{-elim.}} \cdot v_{rev \beta\text{-elim.}})) = (k_{fwd \beta\text{-elim.}} \cdot k_{rev \beta\text{-elim.}}) / (k_p \cdot 1-6 + (k_{fwd \beta\text{-elim.}} \cdot k_{rev \beta\text{-elim.}})) \quad (34)$$

Intermolecular hydrogen abstraction:

$$P_{u \text{ inter}} = P_{\text{inter}} \times P_{\beta\text{-elim.}} \quad (35)$$

$$P_{\text{inter}} = (v_{fwd \text{ inter}} \cdot v_{rev \text{ inter}}) / ((v_{fwd \text{ inter}} \cdot v_{rev \text{ inter}}) + (v_{fwd1-5} \cdot v_{rev1-5}) + (v_{fwd1-2} \cdot v_{rev1-2}) + (v_{fwd \text{ 1-6}} \cdot v_{rev \text{ 1-6}}) + (v_{fwd \text{ HH}} \cdot v_{rev \text{ HH}}) + v_p + v_t) = (k_{fwd \text{ inter}} \cdot k_{rev \text{ inter}}) [P] / ((k_{fwd \text{ inter}} \cdot k_{rev \text{ inter}}) [P] + (k_{fwd1-5} \cdot k_{rev1-5}) + (k_{fwd1-2} \cdot k_{rev1-2}) + (k_{fwd \text{ 1-6}} \cdot k_{rev \text{ 1-6}}) + (k_{\text{HH}} [M] + k_p [M] + k_t [P \cdot])) \quad (36)$$

$$P_{\beta\text{-elim.}} = (v_{fwd \beta\text{-elim.}} \cdot v_{rev \beta\text{-elim.}}) / (v_p \text{ inter} + (v_{fwd \beta\text{-elim.}} \cdot v_{rev \beta\text{-elim.}})) = (k_{fwd \beta\text{-elim.}} \cdot k_{rev \beta\text{-elim.}}) [M] / (k_p \text{ inter} [M] + (k_{fwd \beta\text{-elim.}} \cdot k_{rev \beta\text{-elim.}}) [M]) \quad (37)$$

1–5 backbiting after HH and 1–2 Cl shift:

$$P_{u \text{ 1-5HH-Cl}} = P_{\text{HH}} \times P_{1-2\text{Cl}} \times P_{1-5\text{HH-Cl}} \times P_{\beta\text{-elim.}} \quad (38)$$

$$P_{\text{HH}} = k_{p\text{HH}} / k_p \quad (39)$$

$$P_{1-2\text{Cl}} = (v_{fwd1-2\text{Cl}} \cdot v_{rev1-2\text{Cl}}) / ((v_{fwd1-2\text{Cl}} \cdot v_{rev1-2\text{Cl}}) + v_{p\text{HH}} + (v_{fwd1-6\text{HH}} \cdot v_{rev1-6\text{HH}}) + (v_{fwd1-5\text{HH}} \cdot v_{rev1-5\text{HH}}) + (v_{fwd1-2\text{HH}} \cdot v_{rev1-2\text{HH}}) + (v_{fwd \text{ tr inter}} \cdot v_{rev \text{ tr inter}})) \sim 1; \quad (40)$$

$$v_{p\text{HH}} + (v_{fwd1-6\text{HH}} \cdot v_{rev1-6\text{HH}}) + (v_{fwd1-5\text{HH}} \cdot v_{rev1-5\text{HH}}) + (v_{fwd1-2\text{HH}} \cdot v_{rev1-2\text{HH}}) + (v_{fwd \text{ tr inter}} \cdot v_{rev \text{ tr inter}}) \ll \ll \ll (v_{1-2\text{Cl}}) \quad (41)$$

$$P_{1-5\text{HH-Cl}} = (v_{fwd \text{ 1-5HH-Cl}} \cdot v_{rev \text{ 1-5HH-Cl}}) / ((v_{fwd \text{ 1-5HH-Cl}} \cdot v_{rev \text{ 1-5HH-Cl}}) + (v_{fwd1-6\text{HH-Cl}} \cdot v_{rev1-6\text{HH-Cl}}) + (v_{fwd1-2\text{HH-Cl}} \cdot v_{rev1-2\text{HH-Cl}}) + (v_{fwd \text{ tr inter}} \cdot v_{rev \text{ tr inter}}) + v_{p\text{HH-Cl}} + (v_{fwd \beta\text{-elim.}} \cdot v_{rev \beta\text{-elim.}}) + (v_{fwd2\text{nd1-2Cl}} \cdot v_{rev2\text{nd1-2Cl}}) + v_{t1-5\text{HH-Cl}}) = (k_{fwd1-5\text{HH-Cl}} \cdot k_{rev1-5\text{HH-Cl}}) / ((k_{fwd1-5\text{HH-Cl}} \cdot k_{rev1-5\text{HH-Cl}}) + (k_{fwd1-6\text{HH-Cl}} \cdot k_{rev1-6\text{HH-Cl}}) + (k_{fwd \text{ tr inter}} \cdot k_{rev \text{ tr inter}}) + (k_{p\text{HH-Cl}} [M] + (k_{fwd \beta\text{-elim.}} \cdot k_{rev \beta\text{-elim.}}) [M] + (k_{fwd2\text{nd1-2Cl}} \cdot k_{rev2\text{nd1-2Cl}}) + k_t [P \cdot])) \quad (42)$$

$$P_{\beta\text{-elim.}} = (v_{fwd \beta\text{-elim.}} \cdot v_{rev \beta\text{-elim.}}) / (v_{p1-5\text{HH-Cl}} + (v_{fwd \beta\text{-elim.}} \cdot v_{rev \beta\text{-elim.}}) + (v_{fwd \text{ 1-5HH-Cl}} \cdot v_{rev \text{ 1-5HH-Cl}}) + (v_{fwd1-6\text{HH}} \cdot v_{rev1-6\text{HH}}) + (v_{fwd1-2\text{HH}} \cdot v_{rev1-2\text{HH}}) + v_{t1-5\text{HH-Cl}}) + (v_{fwd \text{ tr inter}} \cdot v_{rev \text{ tr inter}}) = (k_{fwd \beta\text{-elim.}} \cdot k_{rev \beta\text{-elim.}}) [M] / (k_{p1-5\text{HH-Cl}} [M] + (k_{fwd \beta\text{-elim.}} \cdot k_{rev \beta\text{-elim.}}) [M] + k_t [P \cdot] + (k_{fwd \text{ tr inter}} \cdot k_{rev \text{ tr inter}}) [P]) \quad (43)$$

Propagation of chloroallylic radical formed by H abstraction from chloroallylic end group

$$P_{u \text{ allyl}} = P_{HH} \times P_{1,2Cl} \times P_{\beta \text{ elim}} \times P_{p \text{ allyl}} \times P_{H \text{ abstr. allyl}} \quad (44)$$

$$P_{H \text{ abstr. allyl}} = (k_{fwd H \text{ abstr. allyl}} - k_{rev H \text{ abstr. allyl}}) [P] / ((k_{fwd H \text{ abstr. allyl}} - k_{rev H \text{ abstr. allyl}}) [P] + k_{copol} [M]) \quad (45)$$

$$P_{p \text{ allyl}} = (k_{p \text{ allyl}} [M]) / (k_{p \text{ allyl}} [M] + ((k_{fwd1-6 \text{ allyl}} - k_{rev1-6 \text{ allyl}}) + (k_{fwd1-5 \text{ allyl}} - k_{rev1-5 \text{ allyl}}) + (k_{fwd1-2 \text{ allyl}} - k_{rev1-2 \text{ allyl}}) + (k_{fwd \text{ tr inter}} - k_{rev \text{ tr inter}}) [P] + k_t \text{ allyl} [P.]) \quad (46)$$

$$\begin{aligned} \nu_{1-6} &= k_{1-6} [P^\bullet] & \nu_{HH} &= k_{HH} [P^\bullet] [M] & \nu_{1-6HH-Cl} &= k_{1-6HH-Cl} [P^\bullet_{HH-Cl}] \\ \nu_{1-5} &= k_{1-5} [P^\bullet] & \nu_p &= k_p [P^\bullet] [M] & \nu_{pHH-Cl} &= k_{pHH-Cl} [P^\bullet_{HH-Cl}] [M] \\ \nu_{1-2} &= k_{1-2} [P^\bullet] & \nu_{\beta \text{-elim}} &= k_{\beta \text{-elim}} [P^\bullet_{inter}] [M] & k_{HH} &= 5.3 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1} \\ \nu_{tr \text{ inter}} &= k_{tr \text{ inter}} [P^\bullet] [P] & \nu_{1-5HH-Cl} &= k_{1-5HH-Cl} [P^\bullet_{HH-Cl}] & k_{1-6HH-Cl} &\approx k_{1-6} \times (k_{1-5HH-Cl} / k_{1-5}) \\ \nu_{p \text{ allyl}} &= k_{p \text{ allyl}} [P^\bullet] [M] & [P^\bullet] &\sim 0 \end{aligned}$$

$$P_{u \text{ 1-6}} / P_{u \text{ inter}} = (k_{fwd1-6} - k_{rev1-6}) \times ((k_{fwd \text{ inter}} - k_{rev \text{ inter}}) [P] + (k_{fwd1-5} - k_{rev1-5}) + (k_{fwd1-2} - k_{rev1-2}) + (k_{fwd \text{ tr 1-6}} - k_{rev \text{ tr 1-6}}) + (k_{fwdHH} - k_{revHH}) [M] + k_p [M] + k_t [P^\bullet]) / ((k_{fwd1-6} - k_{rev1-6}) + (k_{fwd1-5} - k_{rev1-5}) + (k_{fwd1-2} - k_{rev1-2}) + (k_{fwd \text{ tr inter}} - k_{rev \text{ tr inter}}) [P] + (k_{fwdHH} - k_{revHH}) [M] + k_p [M] + k_t [P^\bullet]) \times (k_{fwd \text{ inter}} - k_{rev \text{ inter}}) [P] = (k_{fwd1-6} - k_{rev1-6}) / (k_{fwd \text{ inter}} - k_{rev \text{ inter}}) [P] \quad (47)$$

$$P_{u \text{ 1-6}} / P_{u \text{ 1-5HH-Cl}} = k_p \times (k_{fwd1-6} - k_{rev1-6}) \times ((k_{fwd1-5HH-Cl} - k_{rev1-5HH-Cl}) + (k_{fwd1-6HH-Cl} - k_{rev1-6HH-Cl}) + (k_{fwd \text{ inter}} - k_{rev \text{ inter}}) [P] + k_{pHH-Cl} [M] + (k_{fwd \beta \text{-elim}} - k_{rev \beta \text{-elim}}) [M] + (k_{fwd2nd \text{ 1-2Cl}} - k_{rev2nd \text{ 1-2Cl}}) / k_{pHH} \times k_{1-5HH-Cl} \times ((k_{fwd1-6} - k_{rev1-6}) + (k_{fwd1-5} - k_{rev1-5}) + (k_{fwd1-2} - k_{rev1-2}) + (k_{fwd \text{ tr inter}} - k_{rev \text{ tr inter}}) [P] + (k_{fwdHH} - k_{revHH}) [M] + k_p [M]) \quad (48)$$

$$P_{u \text{ allyl}} / P_{u \text{ 1-5HH-Cl}} = (k_{p \text{ allyl}} [M]) \times (k_{fwd H \text{ abstr. allyl}} - k_{rev H \text{ abstr. allyl}}) [P] \times ((k_{fwd1-5HH-Cl} - k_{rev1-5HH-Cl}) + (k_{fwd1-6HH-Cl} - k_{rev1-6HH-Cl}) + (k_{fwd \text{ tr inter}} - k_{rev \text{ tr inter}}) [P] + k_{pHH-Cl} [M] + (k_{fwd \beta \text{-elim}} - k_{rev \beta \text{-elim}}) [M] + (k_{fwd2nd \text{ 1-2Cl}} - k_{rev2nd \text{ 1-2Cl}}) / (k_{p \text{ allyl}} [M] + ((k_{fwd1-6 \text{ allyl}} - k_{rev1-6 \text{ allyl}}) + (k_{fwd1-5 \text{ allyl}} - k_{rev1-5 \text{ allyl}}) + (k_{fwd1-2 \text{ allyl}} - k_{rev1-2 \text{ allyl}}) + (k_{fwd \text{ tr inter}} - k_{rev \text{ tr inter}}) [P]) \times ((k_{fwd H \text{ abstr. allyl}} - k_{rev H \text{ abstr. allyl}}) [P] + k_{copol} [M]) \times (k_{fwd1-5HH-Cl} - k_{rev1-5HH-Cl}) \quad (49)$$

Calculations of the ratios of the reaction rates

$$\nu_{1-5-HHCl} / \nu_{tr \text{ inter}} = \frac{k_{fwd \text{ 1-5-HHCl}} - k_{rev \text{ 1-5-HHCl}}}{(k_{fwd \text{ tr inter}} - k_{rev \text{ tr inter}}) [P]} \quad (50)$$

$$\nu_{1-5HHCl} / \nu_{p \text{ 1-5-HHCl}} = \frac{k_{fwd \text{ 1-5-HHCl}} - k_{rev \text{ 1-5-HHCl}}}{k_{p \text{ 1-5-HHCl}} [M]} \quad (51)$$

$$\nu_{1-5} / \nu_{tr \text{ inter}} = \frac{k_{fwd \text{ 1-5}} - k_{rev \text{ 1-5}}}{(k_{fwd \text{ tr inter}} - k_{rev \text{ tr inter}}) [P]} \quad (52)$$

$$\nu_{1-6} / \nu_{tr \text{ inter}} = \frac{k_{fwd \text{ 1-6}} - k_{rev \text{ 1-6}}}{(k_{fwd \text{ tr inter}} - k_{rev \text{ tr inter}}) [P]} \quad (53)$$

$$\nu_{2nd \text{ 1-2Cl}} / \nu_{p \text{ HHCl}} = \frac{k_{fwd \text{ 2nd 1-2Cl}} - k_{rev \text{ 2nd 1-2Cl}}}{k_{p \text{ HHCl}} [M]} \quad (54)$$

$\nu_{tr\ inter}$	rate of intermolecular transfer
$\nu_{1-5-HHCl}$	rate of 1-5 intramolecular transfer (1-5) of 1-2 chlorine shifted head-to-head radical (HHCl)
$\nu_p^{1-5-HHCl}$	propagation rate the radical formed by 1-5 transfer of HHCl radical
$k_{1-5-HHCl}$	rate coefficient of 1-5 intramolecular transfer of HHCl radical
$k_p^{1-5-HHCl}$	rate coefficient of propagation of 1-5 backbitten HHCl radical
[M]	molar concentration of monomer
[P]	molar concentration of polymer

Molar concentrations of polymer and monomer in the polymer rich phase

The solubility of PVC in VCM is extremely low; almost all the polymer is thus located in the polymer rich phase at whole conversion range.

$$[P] = \frac{Xm_{m,0} / M_m}{V_{polymerrich\ phase}} \quad (55)$$

$$[M] = \frac{m_{m,polymer\ rich\ phase,X} / M_m}{V_{polymerrich\ phase}} \quad (56)$$

$$V_{polymerrich\ phase} = V_m + V_p \quad (57)$$

$X < X_f$

At conversion up to X_f only a part of the monomer is contained in the polymer rich phase. The composition of this phase is constant during this period.

$$\phi_{p,X \leq X_f} = \frac{X_f m_{m,0} / \rho_p}{[(1 - X_f)m_{m,0} - m_{m,g,X > X_f} - m_{m,aq,X > X_f}] / \rho_m + X_f m_{m,0} / \rho_p} \quad (58)$$

$$m_{m,polymer\ rich\ phase,X \leq X_f} = V_{m,polymer\ rich\ phase,X \leq X_f} \rho_m \quad (59)$$

$$V_{m,polymer\ rich\ phase,X \leq X_f} = \frac{(1 - \phi_{p,X \leq X_f})}{(\phi_{p,X \leq X_f})} V_p \quad (60)$$

$$V_p = Xm_{m,0} / \rho_p \quad (61)$$

$$X_f = 0.6 \rightarrow \phi_{p,X \leq X_f} = 0.54$$

$X > X_f$

$$\phi_{p,X > X_f} = \frac{Xm_{m,0} / \rho_p}{[(1 - X)m_{m,0} - m_{m,g,X > X_f} - m_{m,aq,X > X_f}] / \rho_m + Xm_{m,0} / \rho_p} \quad (62)$$

$$m_{m, polymer\ rich\ phase, X > X_f} = (1 - X)m_{m,0} - m_{m,g, X > X_f} - m_{m,aq, X > X_f} \quad (63)$$

$$V_{m, polymer\ rich\ phase, X \leq X_f} = m_{m, polymer\ rich\ phase, X \leq X_f} / \rho_m \quad (64)$$

$$V_p = X m_{m,0} / \rho_p \quad (65)$$

$\phi_{p,X}$ volume fraction of polymer in the polymer rich phase at conversion X

V_p volume of polymer in the polymer rich phase

$V_{m, polymer\ rich\ phase, X}$ volume of monomer in the polymer rich phase

References:

1. Deibert, S.; Bandermann, F. *Makromolekulare Chemie-Macromol Chem Phys* **1993**, *194* (12), 3287-3299