Supporting Information

for the article

Effects of Chain Length on the Rates of C-C Bond Dissociation in Linear Alkanes and Polyethylene

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Table 1S. Dependence of C-C bond dissociation constants obtained in molecular dynamics simulations on the critical C-C separation criterion.[a]

Molecule	T / K	N_{Traj}[b]	R_C / nm		
			0.5	0.8	1
PE-1	2300	10	1.00	1.00	1.00
PE-1	3000	10	1.00	1.00	1.00
PE-25	2100	10	1.00	0.92	0.92
PE-25	2700	10	1.00	1.00	1.00
PE-100	2100	20	1.00	1.00	1.00
PE-100	2700	20	1.01	0.99	0.97
PE-1000	2100	20	1.00	1.00	1.00
PE-1000	2700	20	1.03	0.93	0.86

[a] In MD simulations, separation of the two carbon atoms forming a bond by the distance of 0.6 nm was used as the criterion of bond dissociation. Calculations were also performed for selected chain lengths and temperatures using the same trajectories but with the critical bond distance R_C taken as 0.5, 0.8, and 1.0 nm. This table presents ratios $k_{CC}(R_C)/k_{CC}(0.6\ \text{nm})$ averaged over 10 – 20 trajectories as a function of R_C, chain length, and temperature.

[b] Number of trajectories.

Table 2S. C-C bond dissociation rate constants obtained in molecular dynamics simulations using Berendsen and Nose-Hoover methods of temperature control.

Molecule	T / K	$\ln(k / s^{-1})$	
		Berendsen	Nose-Hoover
PE-25	2100	17.80 ± 0.45	16.94 ± 0.60
PE-25	2300	19.71 ± 0.53	19.68 ± 0.67
PE-25	2500	20.30 ± 0.50	20.98 ± 0.46
PE-25	2700	21.65 ± 0.77	21.80 ± 0.34
PE-250	2100	19.63 ± 0.74	20.21 ± 0.44
PE-250	2700	24.13 ± 0.56	24.30 ± 0.42

Table 3S. Properties of the molecules and transition states at selected C-C bond distances.

Reaction PE-1 → 2 CH_3

R(C-C) / nm	0.1528	0.4	0.5	0.6	0.7
Frequencies / cm^{-1}	300.06,[a] 819.91, 819.98, 847.71, 989.49, 989.54, 1338.34, 1386.31, 1386.34, 1403.53, 1403.57, 1444.82, 2864.42, 2871.13, 2976.77, 2976.78, 2982.18, 2982.20	301.02,[a] 810.82, 811.06, 860.31, 860.53, 1295.54, 1327.79, 1349.66, 1350.87, 1358.46, 1359.49, 2789.49, 2867.93, 2974.68, 2974.73, 2975.85, 2975.90	301.02,[a] 809.68, 810.82, 823.24, 848.46, 850.12, 1327.34, 1349.76, 1352.43, 1357.77, 1359.49, 2778.85, 2867.93, 2974.38, 2974.68, 2975.42, 2975.52	136.47, 301.02,[a] 810.81, 811.11, 841.12, 841.45, 1327.41, 1351.94, 1353.52, 1358.36, 1359.49, 2835.65, 2867.94, 2974.18, 2974.68, 2975.21, 2975.33	21.11, 301.02,[a] 810.81, 811.11, 836.14, 836.46, 1327.42, 1352.79, 1354.32, 1358.49, 1359.49, 2843.44, 2867.94, 2974.16, 2974.68, 2975.10, 2975.21
B(1D,ext) / cm^{-1}	2.66	2.66	2.66	2.66	2.66
B(int) / cm^{-1}	10.6	10.6	10.6	10.6	10.6

[a] Torsions

Reaction PE-5 → 2 C_5H_{11}

R(C-C) / nm	0.1528	0.4	0.5	0.6
Frequencies / cm^{-1}	27.1,[a] 55.4,[a] 57.5, 68.1,[a] 109.7,[a] 114.9,[a] 140.7, 149.5,[a] 151.7,[a] 173.0, 230.4,[a] 230.7,[a] 248.8, 325.4, 357.4, 434.4, 441.9, 696.7, 698.9, 706.3, 724.0, 756.1, 802.0, 825.2, 826.8, 855.6, 860.7, 868.5, 875.0, 881.7,	26.9,[a] 52.3,[a] 55.3, 57.7,[a] 100.9, 107.8,[a] 114.6,[a] 129.5,[a] 149.7,[a] 168.5, 230.3,[a] 230.7,[a] 248.5, 319.3, 325.5, 396.2, 441.5, 693.7, 696.5, 706.1, 710.0, 755.9, 769.6, 825.1, 825.3, 855.6, 867.1, 867.5, 868.3, 876.9,	26.9,[a] 47.7,[a] 55.3, 57.7,[a] 89.5, 105.7,[a] 114.6,[a] 127.6,[a] 149.7,[a] 168.8, 230.3,[a] 230.7,[a] 248.5, 313.2, 325.5, 394.6, 441.6, 691.3, 696.5, 706.1, 708.0, 755.9, 765.7, 824.8, 825.3, 855.6, 864.3, 867.1, 868.3, 877.3, 880.8,	26.9,[a] 45.7,[a] 55.3, 57.7,[a] 82.3, 105.0,[a] 114.6,[a] 126.8,[a] 149.7,[a] 168.5, 230.3,[a] 230.7,[a] 248.5, 309.2, 325.5, 394.7, 441.6, 689.3, 696.5, 706.1, 706.8, 755.9, 763.4, 824.0, 825.3, 855.6, 862.4, 864.6, 868.3, 877.7, 880.8,

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B(1D,ext) / cm^{-1}	0.2811	0.23204	0.2121	0.19546
B(int) / cm^{-1}:				
-CH3	5.5846	5.5741	5.5632	5.5529
-C2H5	0.70579	0.63146	0.61676	0.60697
-C3H7	0.55141	0.56212	0.56579	0.56876
-C4H9	0.31118	0.2601	0.2491	0.2415
-C5H11	0.34347	0.3442	0.3443	0.34434
-C4H9	0.31118	0.2601	0.2491	0.2415
-C3H7	0.55141	0.56212	0.56579	0.56876
-C2H5	0.70579	0.63146	0.61676	0.60697
-CH3	5.5846	5.5741	5.5631	5.5529

[a] Torsions

Reaction PE-5 → CH_3 + C_9H_{19}

R(C-C) / nm	0.1528	0.4	0.5	0.6	0.7
Frequencies / cm^{-1}	27.1,[a] 55.4, 57.5,[a] 68.1,[a] 109.7,[a] 114.9,[a] 140.7, 149.5,[a] 151.7,[a] 173.0, 230.4,[a] 230.7,[a] 248.8, 325.4, 357.4, 434.4, 441.9, 696.7, 698.9, 706.3, 724.0, 756.1, 802.0, 825.2, 826.8, 855.6, 860.7, 868.5, 875.0, 881.7, 887.7, 909.1, 914.0, 956.7, 957.9, 967.4, 995.3, 1019.6, 1071.7, 1082.9, 1090.9, 1097.9, 1110.2, 1113.6, 1124.4, 1125.2, 1180.3, 1201.2, 1235.6, 1280.5, 1322.5, 1345.7, 1347.9, 1351.3, 1351.4, 1351.4, 1362.9, 1369.3, 1372.5, 1385.3, 1385.9, 1392.0, 1392.1, 1402.9, 1422.4, 1455.8, 1490.8, 1515.6, 2871.1, 2871.1, 2906.4,	24.2,[a] 45.9, 51.8,[a] 64.4,[a] 102.5,[a] 110.2, 112.6,[a] 147.2,[a] 150.7,[a] 176.0, 213.6, 227.7,[a] 230.6,[a] 327.1, 336.6, 432.6, 439.2, 694.9, 697.4, 703.4, 720.6, 754.0, 802.3, 826.0, 827.6, 839.1, 861.3, 867.1, 871.0, 879.8, 884.8, 893.7, 919.9, 931.7, 963.0, 980.2, 1015.2, 1072.3, 1081.5, 1088.1, 1097.7, 1107.7, 1114.6, 1123.6, 1125.8, 1143.9, 1182.9, 1208.6, 1248.7, 1287.4, 1320.8, 1346.7, 1351.2, 1351.4, 1355.2, 1355.9, 1364.0, 1369.6, 1372.5, 1384.0, 1386.1, 1390.0, 1392.4, 1406.1, 1439.6, 1482.0, 1513.0, 2838.8, 2871.1, 2900.5, 2906.5,	21.7,[a] 39.1, 47.0,[a] 64.4,[a] 101.0,[a] 103.8, 112.7,[a] 146.8,[a] 150.7,[a] 176.4, 209.5, 227.3,[a] 230.6,[a] 326.0, 336.0, 431.9, 439.5, 694.0, 697.3, 703.1, 720.1, 753.6, 802.3, 824.9, 826.0, 832.8, 861.2, 864.7, 871.0, 879.7, 884.3, 892.2, 919.3, 930.7, 962.9, 979.8, 1014.7, 1072.4, 1081.5, 1088.0, 1098.0, 1107.6, 1114.9, 1123.6, 1126.0, 1143.2, 1185.1, 1209.9, 1251.9, 1294.2, 1320.9, 1346.2, 1350.5, 1351.4, 1356.1, 1356.7, 1363.9, 1369.4, 1372.5, 1383.9, 1386.2, 1389.9, 1392.3, 1405.3, 1440.2, 1481.3, 1513.1, 2836.6, 2871.1, 2899.9, 2906.5,	20.9,[a] 35.4, 45.5,[a] 64.5,[a] 100.3,[a] 100.3, 112.7,[a] 146.7,[a] 150.7,[a] 176.6, 207.3, 227.1,[a] 230.6,[a] 325.5, 335.8, 431.8, 439.7, 693.3, 697.2, 702.8, 719.7, 753.2, 802.3, 822.6, 826.0, 828.6, 860.9, 863.6, 870.0, 879.0, 883.9, 890.9, 919.0, 929.8, 962.9, 977.6, 992.3, 1072.4, 1081.6, 1087.9, 1098.2, 1107.5, 1115.2, 1115.8, 1123.5, 1126.1, 1191.0, 1213.5, 1254.7, 1311.4, 1321.2, 1333.2, 1348.6, 1351.4, 1355.6, 1357.2, 1364.8, 1368.2, 1372.6, 1383.6, 1386.2, 1389.7, 1392.0, 1400.5, 1440.6, 1477.5, 1513.4, 2829.5, 2871.1, 2896.3, 2906.5,	20.5,[a] 32.8, 44.7,[a] 64.6,[a] 97.9,[a] 99.9, 112.7,[a] 146.5,[a] 150.7,[a] 170.3, 206.1, 227.0,[a] 230.6,[a] 290.3, 332.0, 395.4, 433.6, 485.2, 692.7, 697.2, 702.7, 719.5, 753.0, 802.3, 821.8, 825.7, 826.0, 861.7, 863.0, 873.2, 881.0, 884.3, 892.1, 918.8, 930.5, 962.9, 980.5, 1053.5, 1072.5, 1081.7, 1087.9, 1098.4, 1107.5, 1115.4, 1123.5, 1126.2, 1190.7, 1204.3, 1223.7, 1269.6, 1319.5, 1345.7, 1350.3, 1351.4, 1355.3, 1357.6, 1365.3, 1369.8, 1372.8, 1383.6, 1386.1, 1389.5, 1392.3, 1401.5, 1436.3, 1479.8, 1513.0, 2854.5, 2870.5, 2890.8, 2906.4,

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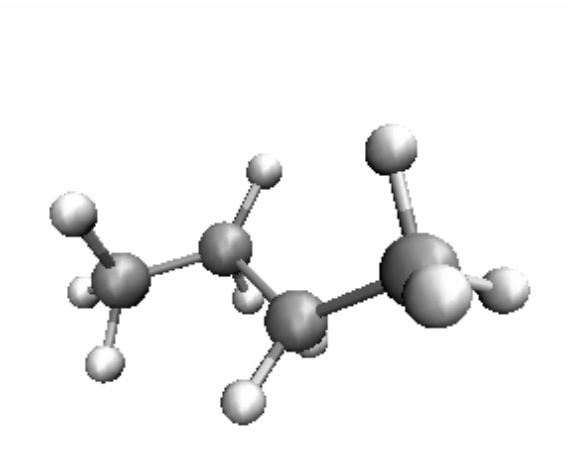
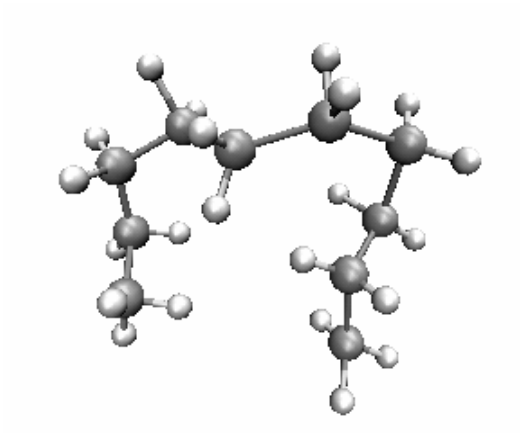
B(1D,ext) / cm^{-1}	0.2811	0.1964	0.16708	0.1439	0.12591
B(int) / cm^{-1}:					
-CH3 (departing)	5.5846	5.5337	5.5139	5.4978	5.485
-C2H5	0.70579	0.22593	0.18947	0.16926	0.15695
-C3H7	0.55141	0.56241	0.57363	0.58467	0.59471
-C4H9	0.31118	0.18722	0.17131	0.16199	0.15626
-C5H11	0.34347	0.35245	0.35763	0.36231	0.36635
-C4H9	0.31118	0.24228	0.23109	0.22431	0.22013
-C3H7	0.55141	0.56242	0.56641	0.56961	0.57215
-C2H5	0.70579	0.62831	0.61252	0.60222	0.59545
-CH3	5.5846	5.5326	5.5128	5.4967	5.4839

[a] Torsions

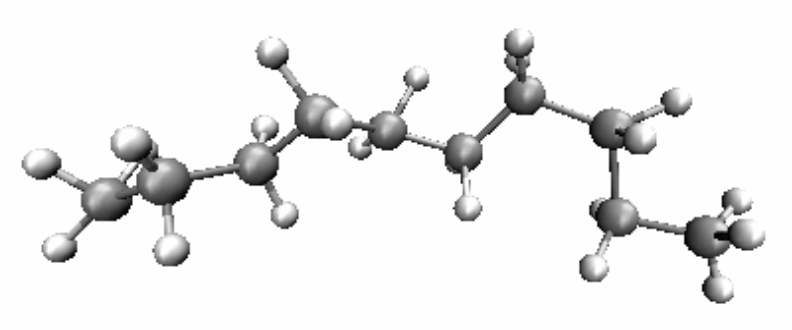
Figure 1S. Snapshots of MD simulations.



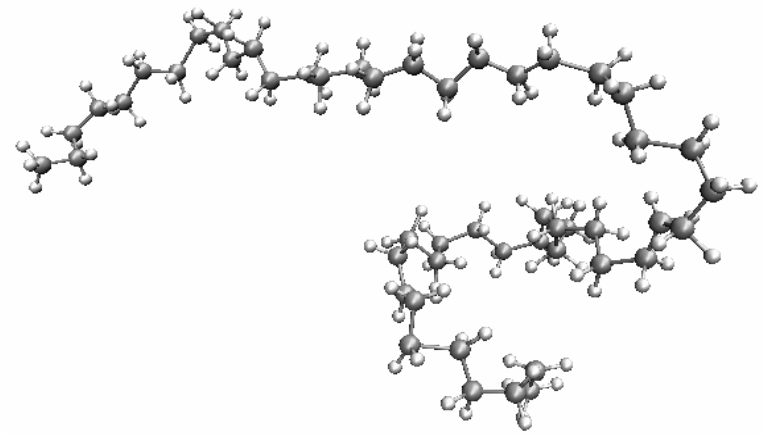
PE-2, 2700 K, 193 ps



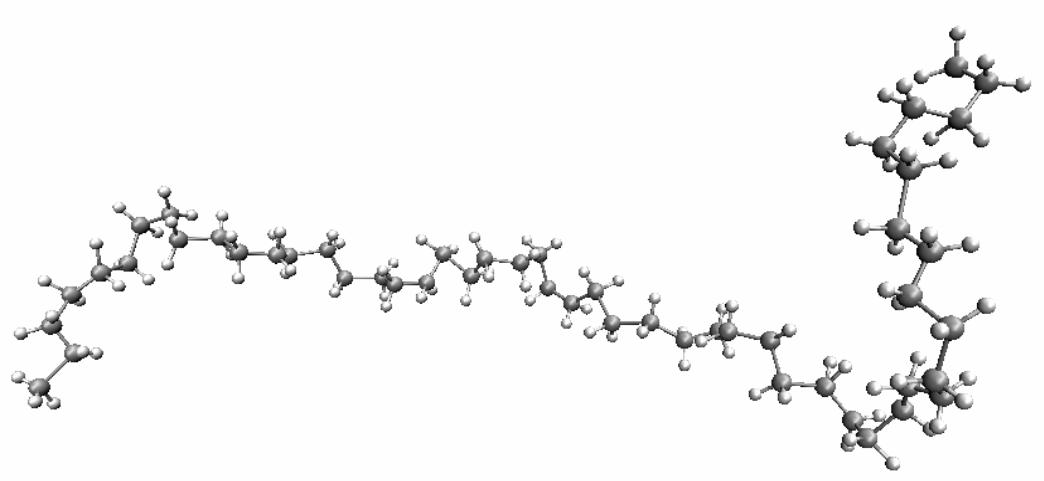
PE-5, 2300 K, 20158 ps



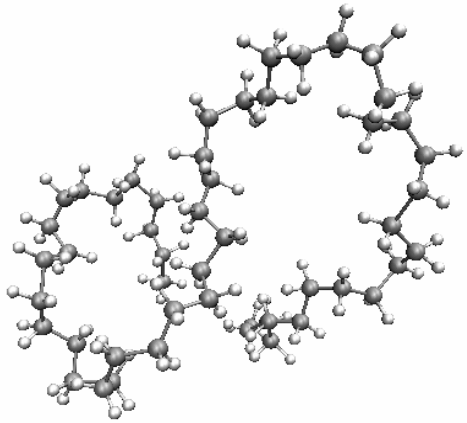
PE-5, 2300 K, 24956 ps



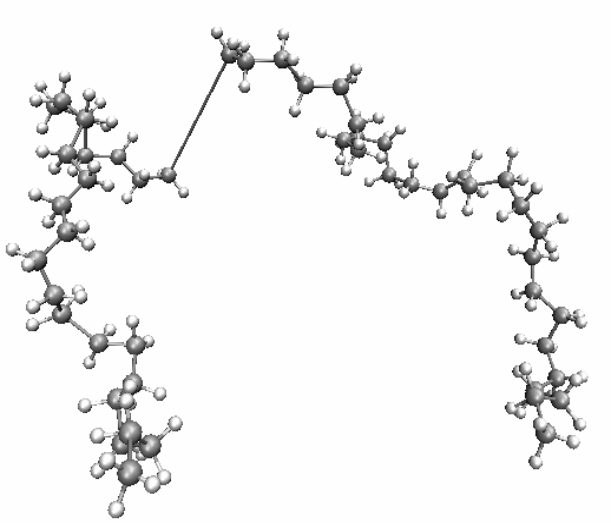
PE-25, 2100 K, 10000 ps



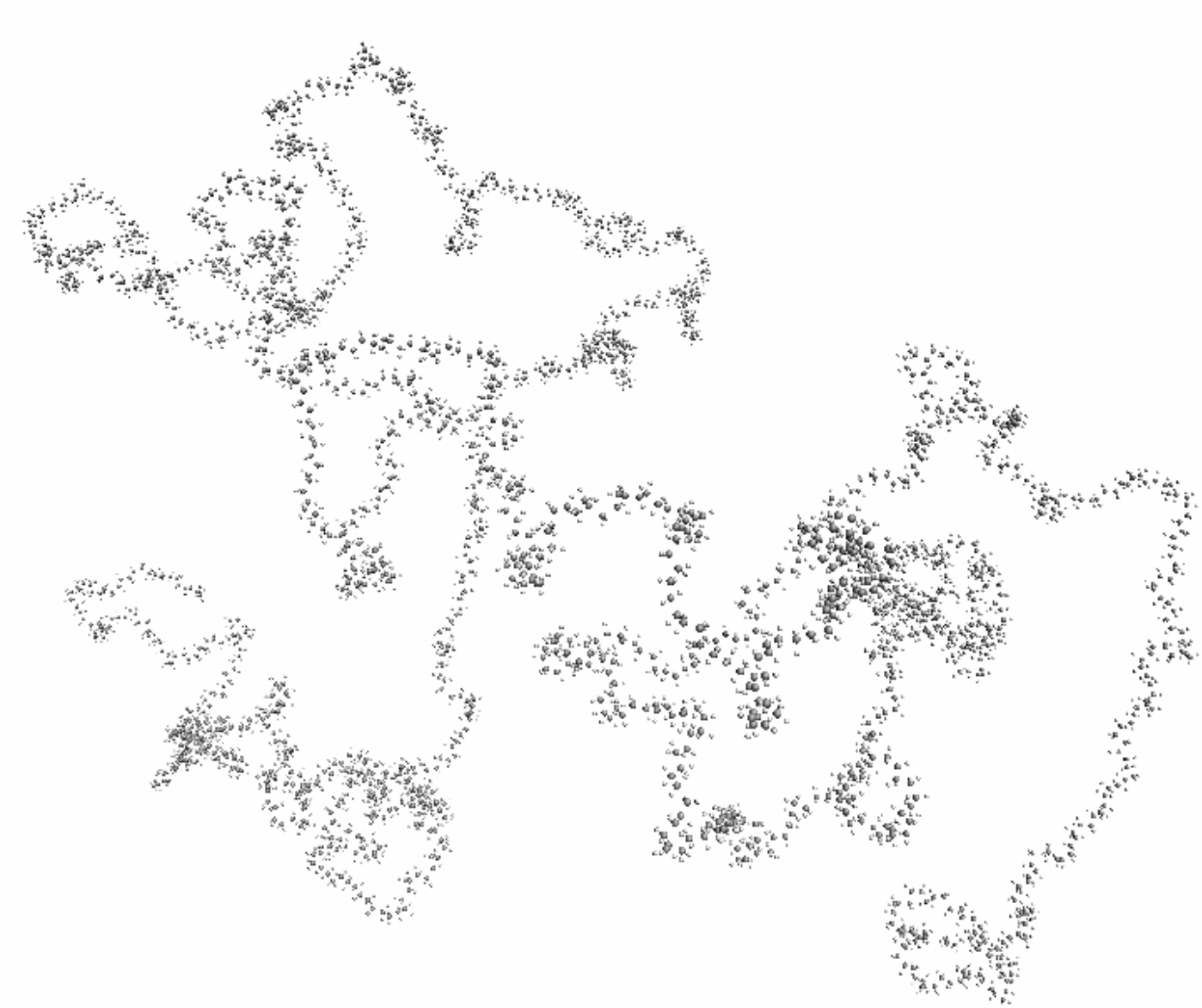
PE-25, 2100 K, 7819 ps



PE-25, 2100 K, 8669 ps



PE-25, 2100 K, 28525.4 ps, one C-C bond is being ruptured



PE-1000, 2300 K, 143.96 ps