

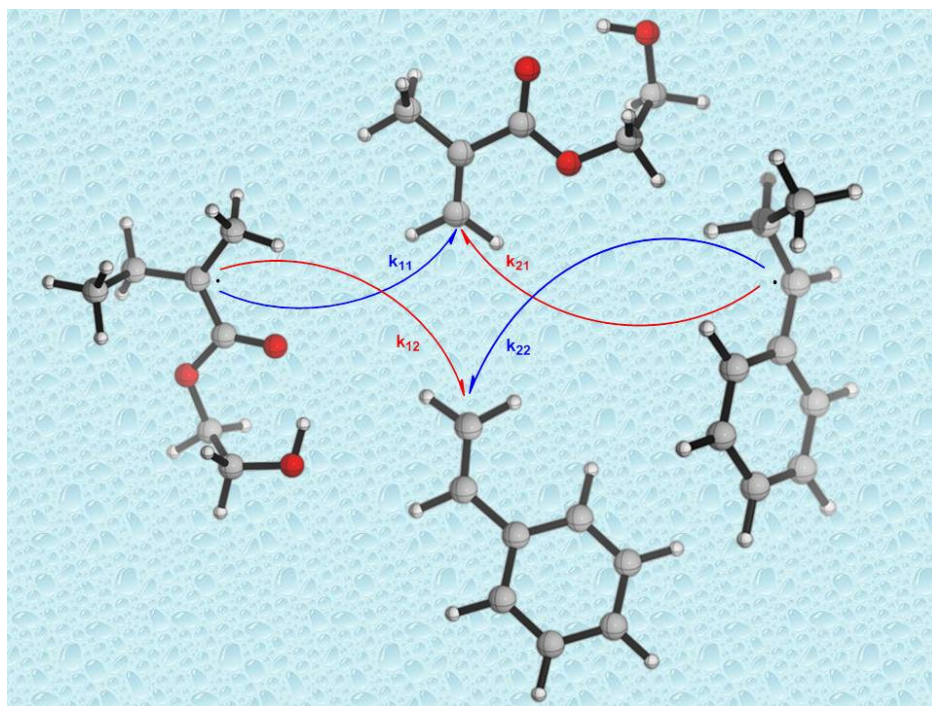
SUPPORTING INFORMATION

Solvent Effects on Free-Radical Copolymerization of Styrene and 2-Hydroxyethyl methacrylate: A DFT Study

T. Furuncuoğlu Özaltın, B. Dereli, Ö. Karahan, S. Salman[‡], V. Aviyente

Boğaziçi University, Department of Chemistry, 34342, Bebek, İstanbul, Turkey

[‡] İstanbul *Bilgi University*, Faculty of Engineering, 34060, Eyüp, İstanbul, Turkey



Propagation Rate Coefficient and Radical Reactivity Calculations in Penultimate Model

Apart from bootstrap effect, other factors such as solvent polarity, radical-solvent and monomer-solvent complexes are demonstrated to affect the free-radical copolymerization.¹ Thus, when the Mayo-Lewis *copolymer composition* equation (also known as the terminal model) is not sufficient to explain the solvent effects, penultimate unit effects are used to explain the solvent dependence of copolymerization. According to penultimate unit model as originally formulated by Merz *et al.*² and used by Fukuda and co-workers,^{3, 4} the solvent modifies the overall propagation rate coefficient, $\langle k_{p, \text{cop}} \rangle$, by affecting the reactivity of the radicals and penultimate units, where a propagation rate coefficient, k_{ijk} ($i, j, k = 1$ or 2), refers to the addition of monomer k to polymeric radical j , with i being the penultimate unit. The overall propagation rate coefficient, $\langle k_{p, \text{cop}} \rangle$, in the penultimate model is:

$$\langle k_{p, \text{cop}} \rangle = \frac{\bar{r}_1 f_1^2 + 2f_1 f_2 + \bar{r}_2 f_2^2}{\left(\frac{\bar{r}_1 f_1}{k_{11}}\right) + \left(\frac{\bar{r}_2 f_2}{k_{22}}\right)} \quad (1)$$

where

$$\overline{k_{11}} = \frac{k_{111}(r_1 f_1 + f_2)}{r_1 f_1 + \frac{f_2}{s_1}} \quad \text{and} \quad \overline{k_{22}} = \frac{k_{222}(r_2 f_2 + f_1)}{r_2 f_2 + \frac{f_1}{s_2}} \quad (2)$$

and the radical reactivity ratios are defined as:

$$s_1 = k_{211}/k_{111} \quad \text{and} \quad s_2 = k_{122}/k_{222} \quad (3)$$

According to the penultimate unit model, the solvent effect on copolymerization may be *explicit* or *implicit*. If the solvent modifies both copolymer composition and propagation rate coefficient, it is known as an *explicit* solvent effect; whereas, if solvent only influences the propagation rate coefficient without changing the copolymer composition (the situation when $\bar{r}_1 = r_1$ and $\bar{r}_2 = r_2$), then it is named as an *implicit* solvent effect following the original terminology used by Fukuda and co-workers.⁴ For instance, in the case of styrene/methyl methacrylate (ST/MMA) system in benzyl alcohol, it is found that the modifications in the

monomer reactivity ratios in solvent are minor, so, the copolymer composition is unchanged, but solvent induces an implicit solvent effect in the propagation rate coefficient.⁵

For example, it is now very well demonstrated that polar solvents significantly affect the copolymerization reactions of donor-acceptor type copolymers through stabilization of their charge-transfer type transition state. The solvent can also affect the reaction through complex formation either with the propagating radical or the monomer.¹ H-bonding interactions are shown to significantly modify the copolymerization kinetics. For instance, the observed solvent dependence of the propagation rate coefficient for ST/HEMA system in alcohols is explained by an implicit penultimate unit effect specific to H-bonding.⁶

1. M. L. Coote, T. P. Davis, B. Klumperman and M. J. Monteiro, *J Macromol Sci R M C*, 1998, **C38**, 567-593.
2. E. Merz, T. Alfrey and G. Goldfinger, *Journal of Polymer Science*, 1946, **1**, 75-82.
3. T. Fukuda, Y. D. Ma and H. Inagaki, *Macromolecules*, 1985, **18**, 17-26.
4. T. Fukuda, K. Kubo and Y. D. Ma, *Prog Polym Sci*, 1992, **17**, 875-916.
5. K. F. ODriscoll, M. L. Monteiro and B. Klumperman, *J Polym Sci Pol Chem*, 1997, **35**, 515-520.
6. K. Liang and R. A. Hutchinson, *Macromolecules*, 2010, **43**, 6311-6320.

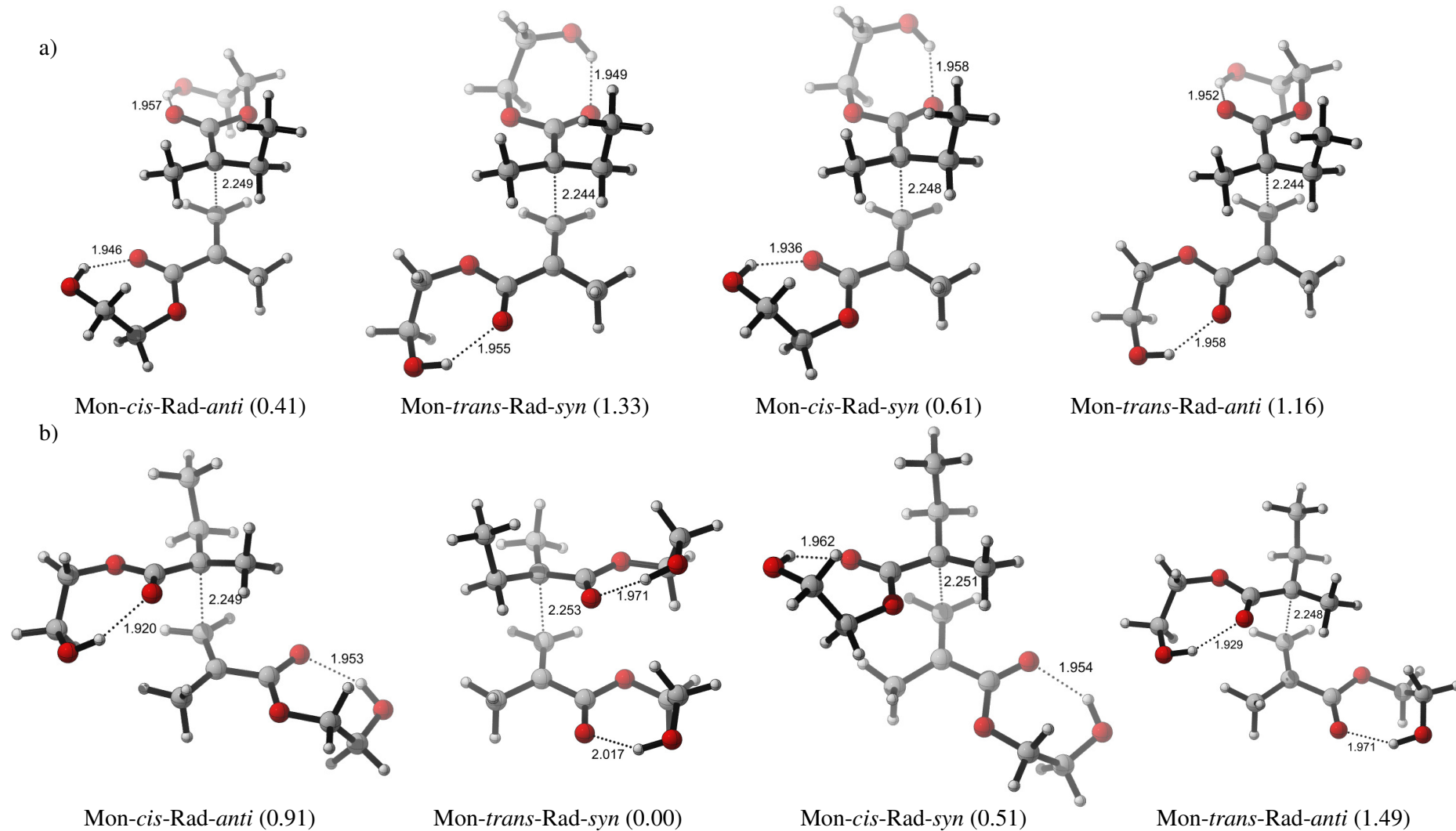


Figure S1. Gas phase optimized geometries of a) Pro-meso and b) Pro-racemo transition states with M06-2X/6-31+G(d,p) methodology (Relative Gibbs Free Energies (kcal/mol) are in parenthesis).

Table S1. Sum of electronic and thermal Gibbs Free Energies for the structures in Figure S1.

	Pro-meso	Pro-racemo
Mon- <i>cis</i> -Rad- <i>anti</i>	-959.8547126	-959.8539292
Mon- <i>trans</i> -Rad- <i>syn</i>	-959.8532521	-959.8553738
Mon- <i>cis</i> -Rad- <i>syn</i>	-959.8543982	-959.8545557
Mon- <i>trans</i> -Rad- <i>anti</i>	-959.8535183	-959.8529964

Table S2. Sample Calculation in Toluene for HEMA-HEMA Homopolymerization (M06-2X/6-31+G(d,p))

T=298.15 K	HF Energy in PCM	Thermal correction to Gibbs Free Energy in PCM (Hartree/Particle)	Zero point Correction in PCM (Hartree/Particle)	COSMORS $\Delta\Delta G$ (kcal/mol)	Bimolecular Correction ($RT\ln(24.5)$) (kcal/mol)
HEMA monomer	-460.1478923	0.123553	0.159206	-6.85231894	1.9
HEMA radical	-500.0206983	0.158193	0.197557	-7.88562909	
HEMA-HEMA-Toluene (TS)	-960.1691186	0.305711	0.358383	-14.31466402	

$$\begin{aligned} \Delta G^\ddagger \left(\frac{\text{kcal}}{\text{mol}} \right) &= ((\text{HF Energy in PCM} + \text{Thermal correction to Gibbs Free Energy in PCM})_{\text{HEMA-HEMA-Toluene}} \\ &\quad - (\text{HF Energy in PCM} + \text{Thermal correction to Gibbs Free Energy in PCM})_{\text{HEMA monomer}} \\ &\quad - (\text{HF Energy in PCM} + \text{Thermal correction to Gibbs Free Energy in PCM})_{\text{HEMA radical}}) * 627.51 \\ &\quad + (\text{COSMORS } \Delta\Delta G)_{\text{HEMA-HEMA-Toluene}} - (\text{COSMORS } \Delta\Delta G)_{\text{HEMA monomer}} - (\text{COSMORS } \Delta\Delta G)_{\text{HEMA radical}} - RT \ln(24.5) \\ &= ((-960.1691186 + 0.305711) - (-460.1478923 + 0.123553) - (-500.0206983 + 0.158193)) * 627.51 \\ &\quad + (-14.31466402) - (-6.85231894) - (-7.88562909) - 1.9 = 13.23 \end{aligned}$$

$$k_p (\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}) = \kappa \frac{kT}{h} \frac{RT}{p^\theta} e^{-\Delta G^\ddagger / RT} = \frac{1.38066 * 10^{-23} * 298.15}{6.62608 * 10^{-34}} * \frac{8.3145 * 298.15}{101035} * e^{\frac{-13.23 * 4.184 * 1000}{8.3145 * 298.15}} = 30.6$$

$$\begin{aligned} E_a \left(\frac{\text{kcal}}{\text{mol}} \right) &= ((\text{HF Energy in PCM} + \text{Zero point Correction in PCM})_{\text{HEMA-HEMA-Toluene}} \\ &\quad - (\text{HF Energy in PCM} + \text{Zero point Correction in PCM})_{\text{HEMA monomer}} \\ &\quad - (\text{HF Energy in PCM} + \text{Zero point Correction in PCM})_{\text{HEMA radical}}) * 627.51 = 0.69 \end{aligned}$$

$$A (\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}) = \frac{k_p}{e^{\frac{-E_a}{RT}}} = \frac{30.6}{e^{1.986 * 298.15}} = 97$$

Table S3. Gas phase standard (at 298 K), activation barriers and stabilization energies
(M06-2X/6-31+G(d,p)).

	Stabilization Energy in DMF (kcal/mol)	Stabilization Energy in Toluene (kcal/mol)	E _a (kcal/mol)
HEMA monomer	-9.24	-2.69	
HEMA radical	-9.46	-2.90	
ST monomer	-3.17	-1.51	
ST radical	-2.48	-1.12	
HEMA-HEMA homopropagation	-20.56	-4.85	2.35
ST-ST homopropagation	-3.77	-1.60	3.97
HEMA-ST(R) copolymerization	-10.44	-3.75	2.96
ST-HEMA(R) copolymerization	-15.21	-3.39	0.47

CALCULATIONS IN BULK (M06-2X/6-31+G(d,p))

REACTANTS

s-trans-HEMA-bulk

C,-1.1626053185,-0.426754434,0.1097698218\H,-0.4109699489,-1.1811660023,0.31247332
91\H,-1.6539150171,0.0420568073,0.9570257488\C,-1.4824657362,-0.0770612017,-1.1396
385931\C,-2.5091023569,0.9593732792,-1.4968030842\H,-3.297963075,0.5255028537,-2.11
81187783\H,-2.0551785319,1.7687669807,-2.0756902547\H,-2.9578877533,1.3765861126,-
0.5940192879\C,-0.8055271018,-0.7212371308,-2.3033311938\O,-1.040943197,-0.4014643
274,-3.4572159571\O,0.0693878112,-1.6704636265,-1.9742042042\C,0.8522023502,-2.2699
867514,-3.0284816057\H,1.5859359391,-2.8643696044,-2.4836852324\H,1.3634701837,-1.
481404251,-3.5893434244\C,0.0459536193,-3.1569725674,-3.9732404367\H,-0.796115539,
-3.5927099533,-3.4163332396\H,0.687940632,-3.9788398058,-4.3013962737\O,-0.3889872
085,-2.5056964121,-5.1496453523\H,-0.7982297515,-1.6701619653,-4.8771219816\\Versio
n=EM64L-G09RevB.01\State=1-A\HF=-460.1509195\

Sum of electronic and zero-point Energies= -459.991913

Sum of electronic and thermal Energies= -459.982009

Sum of electronic and thermal Enthalpies= -459.981065

Sum of electronic and thermal Free Energies= -460.027681

anti-HEMA-R-bulk

C,0.3690844844,-1.1039386524,0.7994226127\C,0.6018379721,-2.5657774809,0.655250706
9\H,0.8976436476,-2.8305152816,-0.3598017769\H,-0.3028863369,-3.1228693415,0.92846
23812\H,1.3883472722,-2.8913234262,1.3490276015\C,0.6843634278,-0.2289403089,-0.31
14714348\O,1.1592544757,-0.6090830355,-1.3829732996\O,0.4043574699,1.0648232013,-0
.0643869879\C,0.7822402368,2.0390991047,-1.0538295014\H,1.839186707,1.9085987319,-
1.3087249778\H,0.6486595099,2.9895558251,-0.5358330403\C,-0.074832918,2.003363681
5,-2.3155202497\H,-0.1419265811,3.0195474602,-2.7144331809\H,-1.09087434,1.6838154
146,-2.0403043736\O,0.4564398841,1.2046189472,-3.3539503367\H,0.7464346762,0.37209
10023,-2.9478417481\C,-0.2536313426,-0.5694604176,2.0483257917\H,0.18506464,0.3989
680041,2.3056502806\H,-0.0479970478,-1.2631259879,2.8703077994\C,-1.7769204212,-0.4
063719919,1.8863133494\H,-2.2207332237,-0.040775451,2.8159925682\H,-2.2464365913,-

1.3621418814,1.6354394612\H,-2.002674601,0.308843884,1.0908773548\\Version=EM64L-G09RevB.01\State=2-A\HF=-500.0239641\

Sum of electronic and zero-point Energies= -499.826587
Sum of electronic and thermal Energies= -499.814597
Sum of electronic and thermal Enthalpies= -499.813653
Sum of electronic and thermal Free Energies= -499.866011

ST-radical-bulk

C,-1.7863767097,0.2486298148,1.5103828172\C,-2.6232145815,-0.2694139662,2.63548446
1\C,-2.4589007288,0.5653662898,3.9191002696\C,-0.4029191923,-0.02707753,1.34188673
26\C,0.310265036,0.5481927531,0.2554707291\C,1.658189466,0.2925122732,0.062004025
6\C,2.3535632215,-0.5452247849,0.9428362836\C,1.6742460072,-1.1210222773,2.0213165
122\C,0.3239136881,-0.8712349474,2.2236582492\H,2.1760966409,0.7451112864,-0.77840
85241\H,-0.1805961639,-1.3263693534,3.0706419608\H,3.4092134265,-0.7455476554,0.79
14845971\H,2.2064795897,-1.7702654672,2.7103908083\H,-3.0869705922,0.1693303975,4.
7224389083\H,-2.7443374594,1.6062124816,3.7406785598\H,-1.418263265,0.5551782213,
4.2570109118\H,-2.2478304191,0.9317314364,0.8015756699\H,-0.2231695409,1.19922293
47,-0.4326688945\H,-3.676008807,-0.2589884203,2.3361282807\H,-2.3693836162,-1.31434
54866,2.852588642\\Version=EM64L-G09RevB.01\State=2-A\HF=-349.3955706\

Sum of electronic and zero-point Energies= -349.222828
Sum of electronic and thermal Energies= -349.214343
Sum of electronic and thermal Enthalpies= -349.213399
Sum of electronic and thermal Free Energies= -349.256830

TRANSITION STATES

HEMA-HEMA-Bulk

C,0.825767371,0.8087044484,-0.4218023441\C,1.3604849642,0.2257933002,0.8489005753\
H,2.2944828772,0.7290195032,1.132606536\H,1.5837636108,-0.8376894091,0.7130115518
\H,0.6551915999,0.3441849665,1.6736813942\C,0.181104005,2.1217152734,-0.3006783065
\O,-0.1071845495,2.6476701789,0.7693839845\O,-0.1164084249,2.6756348313,-1.4858100
569\C,-0.7295759155,3.9802215703,-1.4877157719\H,-0.7213536567,4.2575415155,-2.5423

239516\H,-0.1011017992,4.6761923076,-0.9228272534\C,-2.1568481074,3.9955337776,-0.9
446658035\H,-2.6192296494,3.0166640239,-1.1420167238\H,-2.7263859383,4.7481781707,
-1.4966288116\O,-2.2543356937,4.3513599017,0.4191984829\H,-1.6111678074,3.80523603
44,0.8987827311\C,1.5183082296,0.456090291,-1.7091474529\H,0.8797139346,0.69368766
69,-2.5645517451\H,1.705881439,-0.6228659335,-1.7214149998\C,2.8530902371,1.207281
9098,-1.8483779162\H,3.3454711364,0.9340337352,-2.7852183425\H,3.5308085363,0.9646
138208,-1.0251799984\H,2.6890463931,2.2889670335,-1.8523888828\C,-1.1593415609,-0.2
276334735,-0.6520950092\H,-1.5921713357,0.3152567892,0.1842095811\H,-1.2758785165,
0.1945408389,-1.6464730447\C,-0.8887693336,-1.5593399681,-0.5039305658\C,-0.459603
884,-2.4541133344,-1.6277036526\H,-1.1216369404,-3.3218621446,-1.7105195735\H,0.550
7932168,-2.844348346,-1.4600609435\H,-0.4724625137,-1.9097151336,-2.5741381939\C,-0
.9542342675,-2.1057720975,0.8672380465\O,-1.3074648877,-1.4717606183,1.8528492822\
O,-0.5742460597,-3.3868566783,0.9262080076\C,-0.6418993013,-4.0520499325,2.2039207
988\H,-0.4522556542,-5.0958733557,1.953293167\H,-1.6526763189,-3.9508208637,2.6113
951684\C,0.3902806038,-3.5493646734,3.2106044419\H,1.273051833,-3.1925726354,2.659
4760274\H,0.7045024177,-4.3927027254,3.8311668211\O,-0.0970752211,-2.566900195,4.1
014806843\H,-0.5524380685,-1.8978783709,3.567260062\\Version=EM64L-G09RevB.01\St
ate=2-A\HF=-960.171915\

Sum of electronic and zero-point Energies= -959.813862
Sum of electronic and thermal Energies= -959.791611
Sum of electronic and thermal Enthalpies= -959.790667
Sum of electronic and thermal Free Energies= -959.867839

HEMA-ST(R)-Bulk

C,0.6993607827,0.6255374596,-0.7140977241\H,1.493434856,1.2655828322,-1.082551729
5\H,0.0422717894,1.0459033317,0.0423094577\C,0.7824010363,-0.7337220048,-0.8437118
055\C,-0.1477907941,-1.6874563739,-0.1530966767\H,-0.7240718889,-2.278512629,-0.873
5523207\H,-0.8440980927,-1.1427613401,0.4880143778\H,0.4118562609,-2.3994011734,0
.4624425328\C,1.772829385,-1.3405430715,-1.7408976526\O,1.9047108785,-2.5527157065
, -1.8773842088\O,2.5256510014,-0.4538977957,-2.410252448\C,3.4643223445,-0.95658167
94,-3.3802345488\H,3.809354501,-0.0531839884,-3.8846354196\H,2.9382672939,-1.59574
77405,-4.0970002128\C,4.6479238872,-1.7053196457,-2.7731652795\H,4.860018213,-1.282
4495543,-1.7802958523\H,5.5238898097,-1.5301700133,-3.4036024063\O,4.4789155935,-3

.1074522246,-2.7154876007\H,3.6004498502,-3.2692316189,-2.3356278415\C,-0.61756911
26,1.4115353554,-2.3634446328\H,0.9224918437,3.5732797934,-2.6827627483\C,0.039641
8385,3.7786638974,-2.0816612372\C,-2.2247269926,4.3006738369,-0.5471817241\C,-0.168
3541518,5.0515431629,-1.5658118178\C,-0.8833594089,2.7364410122,-1.8469413399\C,-2.
0198347369,3.0250570253,-1.0608860911\C,-1.3030323043,5.3208561208,-0.7954862175\
H,0.5528065554,5.8385564938,-1.7646730141\H,-2.7476658087,2.2447087239,-0.85728219
95\H,-1.4675942953,6.3153462072,-0.3931751877\H,-3.1084923966,4.5030050903,0.05042
40997\H,0.183107563,1.3494674407,-3.0991805799\C,-1.6839588506,0.362244362,-2.4742
502126\H,-1.2096057293,-0.594581297,-2.7168539059\H,-2.1908285917,0.2212203632,-1.5
112081961\H,-3.4618023932,-0.0890030118,-3.6469727388\C,-2.7170403822,0.7069057052
, -3.5582690556\H,-3.2370856076,1.6401591645,-3.3232315187\H,-2.2297907457,0.829040
4904,-4.5303233232\\Version=EM64L-G09RevB.01\State=2-A\HF=-809.5426856\

Sum of electronic and zero-point Energies= -809.209554
Sum of electronic and thermal Energies= -809.190356
Sum of electronic and thermal Enthalpies= -809.189412
Sum of electronic and thermal Free Energies= -809.260298

SOLUTION PHASE CALCULATIONS – DMF (M06-2X/6-31+G(d,p))

REACTANTS

s-trans-HEMA-DMF

C,-0.9577828619,2.0033672958,3.4338400225\H,-1.2628506146,0.9696718588,3.31663057
44\H,-1.4365401315,2.5899529661,4.2120902084\C,-0.022392322,2.548534282,2.65038706
05\C,0.4482121784,3.9710963263,2.7546404765\H,0.2746427124,4.505975118,1.81626724
66\H,1.5233612845,4.0097653633,2.9523877137\H,-0.0782715693,4.4875070948,3.558810
2324\C,0.6347535225,1.7434734689,1.5775989722\O,1.4889222379,2.1993350946,0.83939
70442\O,0.2042266695,0.478502774,1.5036948688\C,0.7752453369,-0.3528070179,0.48132
09546\H,0.6222740811,-1.3776570265,0.8218433881\H,1.8477170566,-0.1526428941,0.398
6263954\C,0.0653099248,-0.1275399677,-0.8501534551\H,0.1719863145,0.9219018353,-1.
158109684\H,-1.0017129305,-0.3355827087,-0.7253699318\O,0.5724394601,-1.007638475
7,-1.8286808117\H,1.4121906466,-0.6269196628,-2.1628541639\C,3.1277752974,1.304300
7475,-1.9295361571\H,2.5393941188,1.5851397659,-1.0437204912\O,2.8441963966,0.3056

267834,-2.6101983266\N,4.1462526858,2.1329099217,-2.1743355517\C,5.0426347964,1.93
01152978,-3.2998713778\H,5.0182649785,2.8060319226,-3.9548481159\H,4.7225471255,1
.048823556,-3.8529578323\H,6.0653665791,1.7869340082,-2.9386335967\C,4.4046672816,
3.277654073,-1.315132415\H,4.3399629621,4.20342876,-1.8943277512\H,5.4055350458,3.
2006533077,-0.8803908631\H,3.6656717368,3.3040831318,-0.5124136333\\Version=AM64
L-G09RevC.01\State=1-A\HF=-708.5816119\

Sum of electronic and zero-point Energies= -708.317469

Sum of electronic and thermal Energies= -708.299832

Sum of electronic and thermal Enthalpies= -708.298888

Sum of electronic and thermal Free Energies= -708.365671

***anti*-HEMA-R-DMF**

C,-0.7303075157,-0.5335852217,-0.3395986687\C,0.2913056909,-1.298108963,0.42450351
29\H,1.1187241999,-1.5884585263,-0.2361308214\H,-0.1423659159,-2.2312188651,0.8060
504612\H,0.6917279809,-0.7204705086,1.2577371849\C,-0.9904685868,0.8469011976,0.01
79468477\O,-0.4069171373,1.4628715271,0.9073143735\O,-1.958016056,1.4124802626,-0
.7396775979\C,-2.3311756912,2.7586300135,-0.4266949253\H,-2.7901354532,3.154977576
3,-1.33398538\H,-1.4410154614,3.3473660109,-0.1844152225\C,-3.3359476824,2.78054868
36,0.7216644711\H,-2.8892036561,2.3253002101,1.6167482117\H,-4.2093751706,2.183140
5304,0.4416197576\O,-3.7684047353,4.0999201107,0.9734866049\H,-3.0869313549,4.5364
932637,1.5271702039\C,-1.5295409806,-1.2177840394,-1.4012364136\H,-0.9611845641,-2.
0772137282,-1.7715389369\H,-1.7008478955,-0.5397234556,-2.2425845651\C,-2.88806740
57,-1.6986324201,-0.8570777376\H,-3.4448516515,-2.2240702619,-1.6373042137\H,-3.485
7080433,-0.848202231,-0.5175149942\H,-2.7496060045,-2.3830770537,-0.0149398706\N,0
.2979617178,4.4364305281,3.4018212889\C,1.3934497947,3.4794328798,3.388093184\H,2.
3191878876,3.9754655923,3.0815556406\H,1.1645946336,2.6766469501,2.6846369406\H,1
.5329119753,3.0560149153,4.3869962549\C,0.4237506407,5.5806149525,4.2883411631\H,
1.3071224984,6.1659083341,4.0157238451\H,0.53198265,5.2372816908,5.3214601881\H,-
0.4679124266,6.1986870831,4.1979309294\C,-0.7729557376,4.2642221452,2.6223031859\
H,-0.722603034,3.3524301114,2.0089633798\O,-1.7451765096,5.0347797056,2.568631717
7\\Version=AM64L-G09RevC.01\State=2-A\HF=-748.4544659\

Sum of electronic and zero-point Energies= -748.151786

Sum of electronic and thermal Energies= -748.132000
Sum of electronic and thermal Enthalpies= -748.131055
Sum of electronic and thermal Free Energies= -748.203820

ST-monomer-DMF

C,-3.0379373447,1.9640132408,-4.0729398661\C,-3.8356947404,1.784494459,-2.93989337
6\C,-3.5403865983,0.7803579267,-2.0233277952\C,-2.4383220235,-0.0666878009,-2.21883
19729\C,-1.6483696025,0.1223590904,-3.3608084496\C,-1.9424616275,1.1281737758,-4.28
07745102\C,-2.0784798116,-1.144990581,-1.2757384575\C,-2.6807325221,-1.4296226649,-
0.1164945003\H,-0.7928747806,-0.5276011165,-3.5269004164\H,-1.3158461661,1.2567822
832,-5.1579127779\H,-4.1757748549,0.6552866646,-1.1518430171\H,-3.2716708896,2.748
0427324,-4.7862783462\H,-4.6926649057,2.4296132372,-2.7720257513\H,-1.2271201354,-
1.7522386036,-1.5811115779\H,-3.5307047189,-0.8663100189,0.2576573959\H,-2.3289592
781,-2.2496716243,0.5002244186\Version=AM64L-G09RevC.01\State=1-A\HF=-309.5241
276\

Sum of electronic and zero-point Energies= -309.389901
Sum of electronic and thermal Energies= -309.383138
Sum of electronic and thermal Enthalpies= -309.382194
Sum of electronic and thermal Free Energies= -309.421476

ST-radical-DMF

C,-1.7863116236,0.2488160362,1.5108539504\C,-2.6232954863,-0.2695443592,2.63568543
2\C,-2.4598067107,0.5657468877,3.9191316216\C,-0.4027533461,-0.027051563,1.3421412
838\C,0.3103576864,0.5484642335,0.255363587\C,1.6584454903,0.292589634,0.06152661
85\C,2.3541191706,-0.5455277456,0.9421951961\C,1.6748673357,-1.1213989932,2.021022
6877\C,0.3243458307,-0.8716070146,2.2238303889\H,2.17612827,0.7452749211,-0.778990
1292\H,-0.1796995745,-1.3269204986,3.0709930899\H,3.4097161999,-0.745963499,0.7905
524233\H,2.2072058547,-1.7707189329,2.7099505641\H,-3.0895243976,0.1702743719,4.72
13688696\H,-2.7443158906,1.6067243073,3.7398527071\H,-1.4197849741,0.5538268468,4.
2590790865\H,-2.2476035382,0.9323405599,0.8023363995\H,-0.2230733023,1.199686774
8,-0.4326124892\H,-3.6758763196,-0.2588797453,2.3358865281\H,-2.3691416748,-1.31413
12216,2.8538331842\Version=AM64L-G09RevC.01\State=2-A\HF=-349.39628\

Sum of electronic and zero-point Energies= -349.223572
Sum of electronic and thermal Energies= -349.215086
Sum of electronic and thermal Enthalpies= -349.214141
Sum of electronic and thermal Free Energies= -349.257575

TRANSITION STATES

HEMA-HEMA-DMF

C,1.0963352713,2.7528851544,-1.8237409736\C,0.6731375675,1.795169291,-0.7527953079
\C,-0.5250761472,2.1453057521,0.0825649919\C,-0.1901161905,3.2281791689,1.12172413
89\C,1.7385545541,0.9787418866,-0.1580425784\O,1.3447151492,0.342478466,0.96100317
61\C,2.3151002543,-0.4738555466,1.6298130536\C,3.1998175971,0.3831635255,2.5302705
474\O,4.0992156099,-0.4290234498,3.2518617591\O,2.855629171,0.8394023617,-0.641074
0504\O,6.0707301557,-0.8326781665,1.3960774573\C,5.7920523259,-0.3911663323,0.2694
00966\N,6.633365443,-0.3534714014,-0.766985467\C,6.2156969365,0.1897718471,-2.0500
335919\C,7.9981994887,-0.840819396,-0.6617566655\C,-0.1049628278,0.1441378896,-2.06
61015676\C,-0.3917085055,-0.9634359875,-1.3189531454\C,-1.7573372082,-1.0733237134
, -0.7647765906\O,-1.9371724358,-2.2166267827,-0.0830240734\C,-3.2309515289,-2.44243
09145,0.4954864619\C,-4.2121248226,-2.9649930591,-0.5505654025\O,-5.4501635134,-3.2
740281414,0.0520989059\C,0.6123306849,-2.0363475358,-1.0193318655\O,-2.6373674426,
-0.2371538544,-0.9002403813\O,-6.5481677904,-0.7728972414,0.362166463\C,-5.7631842
693,0.1389379784,0.0553580543\N,-5.9910523708,1.4420203468,0.238804331\C,-7.225361
3862,1.9270046984,0.8323207642\C,-4.9938508757,2.4336282007,-0.1335434334\H,1.5108
409435,3.6637480281,-1.370375982\H,0.2385117027,3.0513329238,-2.4332679429\H,1.869
1719662,2.3255581783,-2.4653016389\H,2.9116091883,-1.0234446705,0.8945118121\H,1.7
392415344,-1.1804555813,2.2303715194\H,2.5683884756,0.9147760938,3.2491244717\H,3
.7289164838,1.1335058805,1.9257462206\H,-0.9008611935,1.2551428613,0.593133501\H,-
1.3221383569,2.5025252549,-0.5791784916\H,-1.0760460531,3.4696466821,1.7151373685\
H,0.1555850292,4.1472339353,0.6399641481\H,0.5929185521,2.8802537246,1.8028651283
\H,-0.9104376295,0.808071443,-2.3662754425\H,0.8203803321,0.181013959,-2.634139994
9\H,0.3210746122,-2.9855320522,-1.4823438233\H,0.6887616599,-2.2184091722,0.056951
5235\H,1.5961998399,-1.7521944918,-1.4015379524\H,-3.5955520103,-1.5174992853,0.95
26500003\H,-3.0750826733,-3.1931233314,1.2713011897\H,-3.8110741846,-3.8840014022,
-0.9883894736\H,-4.3289934728,-2.2278121506,-1.3565339317\H,-5.9290060741,-2.431180

213,0.1994014979\H,8.1548291205,-1.2407143544,0.3386324195\H,8.7008780396,-0.02263
90921,-0.8461829434\H,8.1673384516,-1.6261099945,-1.4042146768\H,6.838628298,1.049
4087834,-2.3143010724\H,5.1728979811,0.5066881302,-1.9878282237\H,6.3155654274,-0
.5720606406,-2.8285728672\H,4.7957930677,0.0130108427,0.0368338329\H,-4.784372078
3,-0.0700653678,-0.3998372808\H,-5.4046530978,3.117365815,-0.8821481975\H,-4.116866
9056,1.9297005154,-0.5449116885\H,-4.6956886336,3.0107380657,0.7470300717\H,-7.003
4413061,2.4759625845,1.7523511967\H,-7.8674502512,1.0772794287,1.0580462954\H,-7.7
332996923,2.5984458687,0.1337120352\H,4.8446840129,-0.6509012434,2.6543004154\Ve
rsion=AM64L-G09RevC.01\State=2-A\HF=-1457.0343789\

Sum of electronic and zero-point Energies= -1456.466250
Sum of electronic and thermal Energies= -1456.428290
Sum of electronic and thermal Enthalpies= -1456.427346
Sum of electronic and thermal Free Energies= -1456.544198

ST-ST-DMF

C,-0.6124087272,-0.7566558475,3.3486611203\C,0.0139030839,-0.8072534611,2.08517185
59\C,1.217997626,-1.537055886,1.9767749778\C,1.7738728945,-2.1757682978,3.07856093
28\C,1.1432510935,-2.1087774915,4.3246604734\C,-0.0517983522,-1.3958118198,4.45018
81773\C,-0.5613576682,-0.2020995898,0.9042426682\C,-1.6547036613,0.8243659108,0.97
92747595\C,-1.1447352316,2.1731603232,1.5122677566\C,-1.6844257165,-1.9020106795,-
0.0625358566\C,-0.8129484235,-2.9372407426,-0.2527342197\C,0.135096253,-3.05331797
21,-1.3554883498\C,0.276974035,-2.0590974682,-2.3434384084\C,1.2015648449,-2.202464
9116,-3.3727750921\C,2.0128580341,-3.3377795771,-3.4436229836\C,1.8904498516,-4.329
3117385,-2.468357691\C,0.9668170973,-4.1862351048,-1.4373341515\H,2.7029792326,-2.7
276112936,2.9695383138\H,-1.542530602,-0.2087622809,3.4699970939\H,1.578315651,-2.
6050312439,5.1863660311\H,-0.5494796854,-1.3365906435,5.4137073646\H,0.8783539309
, -4.9606697668,-0.6791699343\H,2.5174747842,-5.2147608939,-2.5108112102\H,-0.337515
1244,-1.1642383392,-2.305849642\H,2.7336284453,-3.4451862034,-4.2479572759\H,1.293
9344546,-1.422003131,-4.1221651948\H,-0.734945151,-3.7006872364,0.5192201403\H,-1.9
331771463,-1.2198419818,-0.8707237081\H,-2.3975784074,-1.9477415616,0.7553125448\
H,-1.9509831458,2.9123349604,1.5292178556\H,-0.3406333315,2.558631133,0.878152203
1\H,-0.7528475569,2.0696504351,2.5285266575\H,0.1155561239,-0.1160403895,0.0542459
152\H,1.7106122783,-1.5961294744,1.008444048\H,-2.0762578813,0.9725593998,-0.02072

03345\H,-2.4758509021,0.4671288656,1.612659163\\Version=AM64L-G09RevC.01\State=2
-A\HF=-658.9141344\

Sum of electronic and zero-point Energies= -658.605562

Sum of electronic and thermal Energies= -658.589694

Sum of electronic and thermal Enthalpies= -658.588750

Sum of electronic and thermal Free Energies= -658.651770

ST-HEMA(R)-DMF

C,0.2560170153,1.7486552839,-0.0056050449\C,0.7211180087,2.5340011874,-1.194827459
4\H,0.0023129173,2.4708482793,-2.0154259883\H,1.6750249617,2.1310200876,-1.5624364
381\H,0.8772461971,3.5839763984,-0.9286402547\C,-0.1869308834,0.3821386563,-0.3033
708993\O,-0.4875143288,-0.0083635333,-1.4199324771\O,-0.3141364046,-0.3873433808,0
.8012379342\C,-0.8975525819,-1.6918045269,0.6566086262\H,-1.583918924,-1.695178426
7,-0.1951943525\H,-1.4592970387,-1.8548518247,1.5800289637\C,0.1692368292,-2.760908
4018,0.5116847204\H,-0.305485541,-3.7357364208,0.6628767851\H,0.9166001645,-2.6235
133386,1.3078349446\O,0.7811238991,-2.7935049764,-0.760038083\H,1.2710134939,-1.95
75449978,-0.8992661188\C,0.8393784209,2.0974040662,1.3368516301\H,0.3602340759,1.5
027130561,2.1186968109\H,0.6170930321,3.1521933796,1.5455772042\C,2.3606233525,1.
8972134255,1.3918547235\H,2.7424358315,2.1570067294,2.3833759269\H,2.8651232671,2
.5325782857,0.6574684799\H,2.6226708501,0.8577911428,1.1765561906\C,-2.691557427,1
.9680690986,-0.5246979537\H,-1.3984905262,3.5582768033,0.0335558113\C,-1.801690833
6,2.5886761695,0.3102162288\H,-1.7623253817,2.3390943934,1.3668579542\H,-4.0132945
856,0.4381419204,-2.2615804075\C,-4.0961197507,0.0637790265,-1.2443257039\C,-4.2965
212503,-0.8977881152,1.3580639967\C,-4.8133594324,-1.1011533589,-0.9899236305\C,-3.
4528690491,0.7637824921,-0.2066903417\C,-3.5743351494,0.2627851258,1.1034166309\C
, -4.9155799044,-1.5898400688,0.3139852383\H,-5.2935792807,-1.6285561553,-1.80848357
1\H,-3.0989186061,0.7829176234,1.9296942668\H,-5.4752978712,-2.4974731191,0.516721
2582\H,-4.3759366281,-1.2678259033,2.3760031415\H,-2.7820478463,2.329061065,-1.547
6165314\C,3.530232513,-1.1785615835,-0.3090700952\H,3.4789384458,-2.1863172771,0.1
319484819\O,2.5611761096,-0.6884279737,-0.9029610817\N,4.7074414648,-0.5725971114,
-0.1249428663\C,5.7974804721,-1.2222821477,0.584316001\H,6.0977361693,-0.615247746
5,1.4430137411\H,6.6568863301,-1.346249882,-0.0811544851\H,5.4744149502,-2.2025905
302,0.9370377592\C,4.9707160496,0.750417788,-0.6673253857\H,5.2446957432,1.4339265

214,0.1420742394\H,4.072190086,1.1129796546,-1.1649252403\H,5.7959765747,0.698234
1403,-1.384083279\\Version=AM64L-G09RevC.01\State=2-A\HF=-1057.9767484\

Sum of electronic and zero-point Energies= -1057.538323
Sum of electronic and thermal Energies= -1057.511746
Sum of electronic and thermal Enthalpies= -1057.510802
Sum of electronic and thermal Free Energies= -1057.598166

HEMA-ST(R)-DMF

C,1.9802989906,1.8483794259,-1.5119527849\H,2.0737267204,0.9808088857,-2.15593910
24\H,2.6437347115,2.6860473397,-1.7094055309\C,0.8177996806,2.0792040582,-0.827228
3745\C,0.540496158,3.3591843939,-0.0928153235\H,-0.3728656469,3.832234057,-0.46882
82452\H,1.3704683404,4.0587141986,-0.2118092625\H,0.3849372638,3.1814730023,0.977
2851821\C,-0.2625894557,1.0780753998,-0.7825950896\O,-1.3353554917,1.2809136491,-0
.2316088852\O,0.0147263937,-0.053783412,-1.4533413375\C,-1.0038031795,-1.060088414
1,-1.5282482359\H,-0.8969589325,-1.5116992714,-2.5177154046\H,-1.9873452489,-0.5906
917005,-1.4444190931\C,-0.8072951623,-2.1164703859,-0.4563050374\H,0.2098557114,-2.
5144964455,-0.5259016219\H,-1.5125956486,-2.9357538682,-0.6633618112\C,3.570998608
1,1.0678996087,-0.1388883841\H,4.3555666465,-0.8428308711,-1.8347762285\C,3.787178
749,-1.2412978268,-0.9972787363\C,2.3401263104,-2.2586047182,1.1524105891\C,3.5591
874709,-2.60773347,-0.9023101086\C,3.3039660223,-0.3495317445,-0.0138885101\C,2.562
3784509,-0.8885598231,1.0577802872\C,2.8396090539,-3.126285201,0.1794022875\H,3.94
7351338,-3.2744941926,-1.666401162\H,2.1632711614,-0.2318926926,1.8253054606\H,2.6
646177132,-4.1947655826,0.2581948838\H,1.7646976057,-2.6505769772,1.9854709228\H,
4.330803274,1.3247167249,-0.8764698073\C,3.4546286377,2.0017821132,1.0302029541\H,
3.5023828608,3.0353097628,0.6701796852\H,2.4775127565,1.8855750026,1.5133882552\H
,4.4832297254,2.4833716933,2.8874561626\C,4.571129015,1.7727495449,2.0607148207\H,
4.5217191192,0.7598780119,2.4713515541\H,5.5552544685,1.9035545704,1.6007320275\N
,5.4706825942,0.2042645556,0.3061138378\C,-5.9499277065,1.4483235583,-0.272509424
2\H,-6.5631974921,1.2398474863,-1.154242199\H,-5.1014059713,2.0673219283,-0.567050
3416\H,-6.5540722104,1.994111241,0.4580950713\C,-6.4771404236,-0.744453068,0.75197
28756\H,-7.0896239575,-1.0639212594,-0.0967962163\H,-7.1247802228,-0.2723159143,1.4
965886244\H,-5.9806649581,-1.6076052185,1.1919873584\C,-4.1636872417,-0.0607729124
,0.4070458694\H,-3.5079314866,0.7384157644,0.0337813211\O,-3.6890737504,-1.1063921

35,0.8745128854\O,-0.9689122211,-1.6170563108,0.8522732807\H,-1.9015979564,-1.3341
685611,0.9417240618\\Version=AM64L-G09RevC.01\State=2-A\HF=-1057.974044\

Sum of electronic and zero-point Energies= -1057.535672
Sum of electronic and thermal Energies= -1057.508903
Sum of electronic and thermal Enthalpies= -1057.507959
Sum of electronic and thermal Free Energies= -1057.597253

SOLUTION PHASE CALCULATIONS – Toluene (M06-2X/6-31+G(d,p))

REACTANTS

s-trans-HEMA-Toluene

C,-1.1572164964,-0.4236393639,0.1142122408\H,-0.4020315187,-1.1744193855,0.3168942
808\H,-1.6486092424,0.0459952396,0.9610284365\C,-1.4809536039,-0.0799225617,-1.1354
71414\C,-2.5121962612,0.950367972,-1.4963080659\H,-3.2990344316,0.5099369676,-2.115
3816028\H,-2.0622717387,1.7571194409,-2.0818178187\H,-2.961737742,1.3712132193,-0
.5954497628\C,-0.8041404597,-0.7252602393,-2.29932608\O,-1.0476627178,-0.414602912
1,-3.4522686804\O,0.0815717552,-1.6653861255,-1.9674641663\C,0.8540181887,-2.267871
616,-3.0264777912\H,1.5881255545,-2.8658240023,-2.4854607403\H,1.365616463,-1.4819
47658,-3.5910365887\C,0.0365125987,-3.1467296411,-3.9722567546\H,-0.8246920245,-3.5
517756971,-3.4200418027\H,0.65851866,-3.9919861751,-4.2796364484\O,-0.3590444176,-
2.5033661722,-5.1625124243\H,-0.7797715658,-1.6679022895,-4.9102258168\\Version=A
M64L-G09RevC.01\State=1-A\HF=-460.1478923\

Sum of electronic and zero-point Energies= -459.988686
Sum of electronic and thermal Energies= -459.978811
Sum of electronic and thermal Enthalpies= -459.977867
Sum of electronic and thermal Free Energies= -460.024339

anti-HEMA-R-Toluene

C,0.3705829501,-1.1021656182,0.8031140467\C,0.594265195,-2.5645211023,0.6476023082
\H,0.9135174575,-2.8164689035,-0.3636770688\H,-0.3225554649,-3.1176541028,0.888368
8681\H,1.3593523742,-2.9071867032,1.3567672834\C,0.6857387692,-0.2237850141,-0.306

7532634\O,1.1469231806,-0.602820359,-1.3818189609\O,0.419577796,1.0720302416,-0.04
92655932\C,0.7816907799,2.039989303,-1.0500414158\H,1.8382963456,1.9178935609,-1.3
108175246\H,0.6412460081,2.9932869902,-0.5385349905\C,-0.0788828147,1.9791093052,-
2.3111274314\H,-0.2021578381,2.9955314359,-2.6959769284\H,-1.0764114062,1.60468562
42,-2.0345181057\O,0.4868164503,1.2290792484,-3.3625363449\H,0.7793028216,0.385760
0722,-2.9835429881\C,-0.2503918738,-0.5701259624,2.0541472574\H,0.1948339922,0.394
1085886,2.3165059555\H,-0.0510203596,-1.2689498135,2.8736410352\C,-1.7719362508,-0.
3936608387,1.8909150016\H,-2.2161519893,-0.0318790295,2.821967145\H,-2.2492627217,
-1.3431714927,1.6307287772\H,-1.9893744013,0.3299165695,1.100851937\Version=AM6
4L-G09RevC.01\State=2-A\HF=-500.0206983\

Sum of electronic and zero-point Energies= -499.823141
Sum of electronic and thermal Energies= -499.811168
Sum of electronic and thermal Enthalpies= -499.810224
Sum of electronic and thermal Free Energies= -499.862505

ST-monomer-Toluene

C,-3.0303546917,1.9717497047,-4.0640137692\C,-3.8454064138,1.7720753338,-2.9476222
359\C,-3.5602968256,0.7562051242,-2.0417845109\C,-2.4502362791,-0.080665822,-2.2296
782619\C,-1.6459517,0.1254975964,-3.3577088908\C,-1.929305524,1.1430233756,-4.26697
55295\C,-2.1005041464,-1.1665920553,-1.2927214861\C,-2.654962545,-1.4017552611,-0.0
999767321\H,-0.785770818,-0.5193256124,-3.5197276251\H,-1.2903911936,1.2861712072
, -5.1329417468\H,-4.2126703139,0.6078941024,-1.1865806969\H,-3.2566514449,2.764251
0715,-4.7703510078\H,-4.7101132792,2.4085684539,-2.7865181458\H,-1.2986202818,-1.82
17480712,-1.6311788541\H,-3.4465980594,-0.7808818379,0.309163079\H,-2.3201664836,-
2.2324663098,0.5116174138\Version=AM64L-G09RevC.01\State=1-A\HF=-309.5217826\

Sum of electronic and zero-point Energies= -309.387513
Sum of electronic and thermal Energies= -309.380734
Sum of electronic and thermal Enthalpies= -309.379790
Sum of electronic and thermal Free Energies= -309.419305

ST-radical-Toluene

C,-1.7866697777,0.2488663962,1.5090425514\C,-2.6234978719,-0.2684910008,2.63449991
85\C,-2.4564300273,0.5637033727,3.9193294253\C,-0.4033460093,-0.0266839212,1.34135
50863\C,0.3101158941,0.5475068877,0.2553562143\C,1.6577393644,0.2920517958,0.0628
02203\C,2.3524175101,-0.5445760165,0.9444227991\C,1.6728696008,-1.1196146818,2.022
5238175\C,0.3228420257,-0.8698260096,2.2237313329\H,2.1760405453,0.7439962277,-0.7
776671374\H,-0.1824828172,-1.3244900281,3.070453109\H,3.4081484787,-0.7448614513,0
.7938088973\H,2.2048237037,-1.7683971504,2.7121991169\H,-3.0815565001,0.166227727
9,4.724383135\H,-2.7427463443,1.6047610468,3.7438443123\H,-1.4146122382,0.55511739
07,4.2532943119\H,-2.2483123576,0.9305460074,0.7990196869\H,-0.2232796618,1.197741
4923,-0.4335083031\H,-3.6767711108,-0.2570539578,2.3363683839\H,-2.3712934066,-1.31
45231279,2.8487401391\\Version=AM64L-G09RevC.01\State=2-A\HF=-349.3942228\

Sum of electronic and zero-point Energies= -349.221410

Sum of electronic and thermal Energies= -349.212930

Sum of electronic and thermal Enthalpies= -349.211986

Sum of electronic and thermal Free Energies= -349.255402

TRANSITION STATES

HEMA-HEMA-Toluene

C,2.6477116072,-0.4030498998,-1.3499845965\C,2.2436722156,0.8877132256,-0.70119079
04\C,2.8825508032,2.1582935882,-1.1797441754\C,4.368986479,2.2197014521,-0.7922572
702\C,1.829061428,0.8740617456,0.7058479036\O,1.5598678302,-0.3595390379,1.1614164
9\C,1.0597418646,-0.4819628688,2.5047449247\C,2.0901227338,-0.1457689781,3.5820945
34\O,1.9960441066,1.1704341821,4.0788651015\O,1.7093080287,1.8819956859,1.3923211
117\C,0.1462017828,1.0435130533,-1.5066016893\C,-0.35885603,2.2733772868,-1.193763
8764\C,-1.1173513822,2.4825372893,0.0574337645\O,-1.2752959388,1.3766091209,0.7966
373738\C,-2.076570531,1.4980175453,1.9893597801\C,-1.4586596788,2.4051611503,3.058
7697785\O,-2.0555126438,3.6814460239,3.1262189371\C,-0.1583988511,3.4954681887,-2.
0366479592\O,-1.5803988121,3.5667062932,0.3757330323\H,3.5931286365,-0.7642709998
, -0.9235868943\H,2.8017709613,-0.2571420335,-2.4231148228\H,1.9064209181,-1.190156
5417,-1.1962821959\H,0.764090723,-1.5301955333,2.5689021759\H,0.1785812262,0.15632
58078,2.6201357169\H,3.0942811248,-0.3628116718,3.1877095262\H,1.9224294276,-0.803
7238594,4.4392809024\H,1.9955699467,1.7673780222,3.3153201097\H,2.3598478141,3.01

37444827,-0.7445380005\H,2.7860857798,2.2196534989,-2.2705486625\H,4.4842620677,2.
1758138852,0.2948095495\H,4.81348732,3.1547221746,-1.1426719829\H,4.9296544336,1.
3908425103,-1.2342501966\H,-0.1602759735,0.166497297,-0.9446169478\H,0.5667288745,
0.8788418079,-2.4953965719\H,0.3494838847,4.283510509,-1.4706787955\H,-1.123316321
3,3.908989881,-2.3480910891\H,0.4285298632,3.2594515588,-2.9265532434\H,-2.1593092
017,0.4675812635,2.3396942902\H,-3.071461861,1.8668163705,1.719541093\H,-0.3753346
09,2.4690094081,2.8816134835\H,-1.609100078,1.9489754893,4.0412735045\H,-1.9769709
693,4.0701496261,2.242609677\Version=AM64L-G09RevC.01\State=2-A\HF=-960.169118
6\

Sum of electronic and zero-point Energies= -959.810735
Sum of electronic and thermal Energies= -959.788540
Sum of electronic and thermal Enthalpies= -959.787596
Sum of electronic and thermal Free Energies= -959.863407

ST-ST-Toluene

C,-0.6131879293,-0.7499985376,3.3361743541\C,0.0072252769,-0.8051309895,2.07087168
39\C,1.2022607002,-1.5474719464,1.9559507664\C,1.7543832195,-2.1944712216,3.053935
435\C,1.129447674,-2.1234133438,4.3019015091\C,-0.0560268019,-1.3975127003,4.43386
49773\C,-0.567749848,-0.1952215981,0.8925218976\C,-1.6563607934,0.8357708011,0.972
7468096\C,-1.1407330122,2.1828923987,1.5043059653\C,-1.6976469668,-1.8969519985,-0
.0738546325\C,-0.8212685886,-2.9295298178,-0.2494021077\C,0.1361695678,-3.05194513
01,-1.3425511447\C,0.2626900434,-2.0827236546,-2.3560041799\C,1.2002781628,-2.2300
868945,-3.3720205731\C,2.0402807914,-3.3452221613,-3.4039938863\C,1.9331047842,-4.3
121403821,-2.4036501163\C,0.9961205977,-4.1647073453,-1.3863095911\H,2.6766742498,
-2.7565663739,2.9397589382\H,-1.5360427298,-0.1908661767,3.4624370384\H,1.56197263
81,-2.6266071087,5.1608101829\H,-0.5491392542,-1.3346899296,5.3994975106\H,0.91903
77122,-4.9194206087,-0.607348534\H,2.5824586318,-5.1823285877,-2.41603452\H,-0.3768
623194,-1.2047380972,-2.3494977451\H,2.7711538231,-3.4562841,-4.1986451424\H,1.279
6744156,-1.4690095666,-4.1426089085\H,-0.7415479224,-3.6803600706,0.5343400923\H,-
1.9444977394,-1.2222294593,-0.8888063625\H,-2.4143226073,-1.937646987,0.7409968091
\H,-1.9455226845,2.9235121152,1.5327625249\H,-0.3426123899,2.5698102701,0.86368067
17\H,-0.7357734871,2.0749635065,2.5147487392\H,0.1072477074,-0.1116146761,0.040634
2733\H,1.6891578068,-1.6117147083,0.9850603018\H,-2.0849010999,0.9852733894,-0.024

5897871\H,-2.4756846288,0.4800366908,1.6098227504\\Version=AM64L-G09RevC.01\State=2-A\HF=-658.9103122\

Sum of electronic and zero-point Energies= -658.601851

Sum of electronic and thermal Energies= -658.585944

Sum of electronic and thermal Enthalpies= -658.585000

Sum of electronic and thermal Free Energies= -658.648470

ST-HEMA(R)-Toluene

C,4.5799134404,-1.6626383722,3.7778136522\C,4.6167736612,-2.8528033009,4.4979577572\C,3.4481836249,-3.3662777574,5.061536061\C,2.2428848935,-2.6800524668,4.8942294832\C,2.2066303099,-1.48781369,4.1808416011\C,3.3780025408,-0.9517815998,3.6146323837\C,3.3881125535,0.312957989,2.8837496722\C,2.4396913577,1.2921885169,2.9971893743\C,3.0518266607,2.712784498,4.6318401213\C,3.9809268843,3.6277173792,3.8902894434\C,3.7093067521,1.7133041252,5.473528466\O,2.8653184323,1.0444034418,6.2774775635\C,3.4002749569,-0.0568359527,7.038164699\C,4.3045242401,0.3769927094,8.1885418046\O,5.6786278119,0.3948901195,7.8678714325\C,1.7009988193,3.2394881125,5.0315723346\C,1.8082155836,4.3090581916,6.1299875472\O,4.9083356615,1.4619097366,5.420797795\H,4.7691356289,3.0624353348,3.3872718274\H,4.4760279467,4.323183708,4.5812462486\H,3.4302485776,4.2216034627,3.1543922197\H,3.9376098054,-0.7370140375,6.3679030905\H,2.5076652192,-0.5554034049,7.4198623203\H,4.1904879566,-0.3407036152,9.006626499\H,3.9617592621,1.3570465617,8.5547367869\H,5.7615378908,0.8136585937,6.9964384775\H,1.0693579347,2.4201300425,5.3856897714\H,1.2167806031,3.6735829642,4.1478022834\H,0.8152094992,4.6701937111,6.4113420124\H,2.3975851444,5.1663598484,5.7919821863\H,2.2865350851,3.895817926,7.023514003\H,2.4524756036,2.1341091431,2.311626895\H,1.4957765194,1.0946835122,3.4975166813\H,5.4942543252,-1.2565270868,3.3534724402\H,5.5584511515,-3.3778984019,4.6235646209\H,1.259410386,-0.9726478157,4.0527850032\H,3.4749556765,-4.2954833254,5.6219544357\H,1.3272943306,-3.0793716563,5.3201390554\H,4.2818822689,0.5172068554,2.2971459502\\Version=EM64L-G09RevB.01\State=2-A\HF=-809.5423816\

Sum of electronic and zero-point Energies= -809.208996

Sum of electronic and thermal Energies= -809.190030

Sum of electronic and thermal Enthalpies= -809.189086

Sum of electronic and thermal Free Energies= -809.257761

HEMA-ST(R)-Toluene

C,0.6862063502,0.6162796737,-0.707458844\H,1.4782007103,1.2621228188,-1.070052927
8\H,0.0264568014,1.030221036,0.0503405184\C,0.7778356888,-0.741279615,-0.844876624
9\C,-0.1423587618,-1.7077661758,-0.1591975099\H,-0.7130389117,-2.300793904,-0.88242
663\H,-0.8422332644,-1.1745959922,0.4879084706\H,0.4262851517,-2.4192676009,0.4483
372563\C,1.7726226864,-1.3368294622,-1.7469601734\O,1.9206667893,-2.5447591902,-1.8
82887472\O,2.5079784841,-0.438081953,-2.4229744822\C,3.4621982123,-0.9369591631,-3.
3783367122\H,3.8090597535,-0.0315292484,-3.8785321692\H,2.950676855,-1.5807290929,
-4.101721811\C,4.6389829945,-1.6865057991,-2.7535612576\H,4.8043591593,-1.29520010
89,-1.7383965968\H,5.5361066374,-1.4721121828,-3.3412968304\O,4.4977198511,-3.0891
276673,-2.7571046437\H,3.6269217338,-3.2866189796,-2.3786289984\C,-0.6251373649,1.4
031285789,-2.3579505401\H,0.9296928717,3.5514300707,-2.688569261\C,0.0486537951,3
.7665516977,-2.0881441186\C,-2.2114232615,4.3133790578,-0.5578989259\C,-0.14951551
71,5.0430468983,-1.578707049\C,-0.8819649532,2.7325160641,-1.8491468885\C,-2.016153
3557,3.0340661643,-1.0652240465\C,-1.2820635411,5.3248606528,-0.810485492\H,0.5776
566535,5.8235363787,-1.7812418748\H,-2.7506490615,2.2605628064,-0.8592853782\H,-1.
4390805489,6.3226102668,-0.4133946106\H,-3.0939711452,4.5256413714,0.0380350001\
H,0.1750475841,1.3315219983,-3.0934787815\C,-1.6987047939,0.3604408728,-2.46362037
49\H,-1.2308236973,-0.6008283878,-2.7016108633\H,-2.204223668,0.2263450181,-1.49858
13498\H,-3.4846770563,-0.0827570374,-3.6283676321\C,-2.7319536743,0.7064924423,-3.5
468884468\H,-3.2416876837,1.6469388163,-3.3183448376\H,-2.2466655031,0.8170468765,
-4.5212650908\\Version=AM64L-G09RevC.01\State=2-A\HF=-809.5384601\

Sum of electronic and zero-point Energies= -809.205113

Sum of electronic and thermal Energies= -809.185945

Sum of electronic and thermal Enthalpies= -809.185001

Sum of electronic and thermal Free Energies= -809.255882

GAS PHASE CALCULATIONS (M06-2X/6-31+G(d,p))

REACTANTS

s-trans-HEMA-Gas

C,-1.1576541224,-0.4264890268,0.1178603669\H,-0.4026348464,-1.1776983034,0.3192154
238\H,-1.6494410756,0.0427308589,0.9647328087\C,-1.480321002,-0.0827677034,-1.13160
99792\C,-2.5106145315,0.9471544716,-1.4954805571\H,-3.2942803212,0.506259624,-2.118
0300926\H,-2.0587671345,1.7521758306,-2.081841651\H,-2.9631588241,1.3694537546,-0.
596628146\C,-0.8041110095,-0.7285789841,-2.2964138365\O,-1.0573878424,-0.426935332
9,-3.4477223055\O,0.0936900894,-1.6582892623,-1.9624953369\C,0.8564205915,-2.261858
6916,-3.0266071626\H,1.595647825,-2.8579675681,-2.4896641955\H,1.3621932102,-1.476
9593741,-3.5982142567\C,0.0306029903,-3.1391665125,-3.9697792942\H,-0.8420745438,-
3.5213240287,-3.4175882995\H,0.6385532388,-4.0012476534,-4.2597474144\O,-0.3370957
081,-2.5082426797,-5.1702431971\H,-0.7745659837,-1.6762514188,-4.9387438746\
Version=AM64L-G09RevC.01\State=1-A\HF=-460.1439501\

Sum of electronic and zero-point Energies= -459.984539

Sum of electronic and thermal Energies= -459.974691

Sum of electronic and thermal Enthalpies= -459.973747

Sum of electronic and thermal Free Energies= -460.020086

anti-HEMA-R-Gas

C,0.3634418221,-1.1031154302,0.8030200578\C,0.5764875472,-2.5654645262,0.630346885
4\H,0.9011310053,-2.8028934542,-0.3829496397\H,-0.3467593201,-3.1154490327,0.85491
22571\H,1.33345566,-2.9261795234,1.339377396\C,0.6765991618,-0.2180460369,-0.30411
08294\O,1.1362843644,-0.5914372375,-1.3786658899\O,0.408072183,1.0763693871,-0.037
5847325\C,0.7603033876,2.0436520359,-1.0419029267\H,1.823435919,1.9458303067,-1.28
64350725\H,0.5881953505,2.996785293,-0.5390587514\C,-0.0723187678,1.9460005555,-2.
3227038718\H,-0.2623067753,2.9582656659,-2.691903861\H,-1.0463508045,1.4975668635,
-2.070692229\O,0.565666773,1.2663322553,-3.3739599554\H,0.8543537502,0.4091278986,
-3.0266861505\C,-0.2422310008,-0.5751336145,2.0634898605\H,0.2183928404,0.38099338
46,2.3299776078\H,-0.0454215373,-1.2832447259,2.8760453845\C,-1.7620347997,-0.37404
22399,1.9159148916\H,-2.1939539712,-0.0173938182,2.8548425911\H,-2.2567212355,-1.3

125021723,1.6476974482\H,-1.9737205522,0.3629801658,1.1370285298\\Version=AM64L-G09RevC.01\State=2-A\HF=-500.0164953\

Sum of electronic and zero-point Energies= -499.818780
Sum of electronic and thermal Energies= -499.806797
Sum of electronic and thermal Enthalpies= -499.805853
Sum of electronic and thermal Free Energies= -499.858263

ST-monomer-Gas

C,-3.0243558344,1.9782263187,-4.0551050876\C,-3.8547515045,1.7599884736,-2.9543920156\C,-3.5781679253,0.7333003541,-2.0587346035\C,-2.4608816466,-0.0942164962,-2.2400310156\C,-1.6435476696,0.1278145587,-3.3550060342\C,-1.9179646878,1.1561676899,-4.2538525603\C,-2.1203972397,-1.1858137525,-1.3070047114\C,-2.6308885405,-1.3757164831,-0.0874947737\H,-0.7786972723,-0.5116489768,-3.5132334005\H,-1.2681952272,1.3131493597,-5.1092739823\H,-4.2445380642,0.5636987173,-1.2183760925\H,-3.2440670193,2.7786848638,-4.7544750579\H,-4.7262155039,2.3886720441,-2.7992057026\H,-1.3649228341,-1.8819117445,-1.6695091573\H,-3.3676748711,-0.7052674739,0.3450788018\H,-2.3127351595,-2.2131254528,0.5236153931\\Version=AM64L-G09RevC.01\State=1-A\HF=-309.519985\

Sum of electronic and zero-point Energies= -309.385611
Sum of electronic and thermal Energies= -309.378867
Sum of electronic and thermal Enthalpies= -309.377922
Sum of electronic and thermal Free Energies= -309.417027

ST-radical-Gas

C,-1.7867121225,0.2485942431,1.5079772412\C,-2.6235777916,-0.2677521829,2.6338739516\C,-2.4545743153,0.5629099509,3.9192851969\C,-0.4035752536,-0.0267555191,1.3409949252\C,0.3100243197,0.5469850684,0.2556861328\C,1.6572844327,0.2920483192,0.063862556\C,2.3513098831,-0.5439080183,0.9457347278\C,1.6717413632,-1.1187959602,2.0231757222\C,0.3220392494,-0.8693388666,2.2234614133\H,2.1759085893,0.7438384679,-0.7764039898\H,-0.1840041533,-1.3242725401,3.0695725788\H,3.4071139053,-0.743943357,0.7956943287\H,2.2035022652,-1.767505944,2.7129796814\H,-3.0770633706,0.1647436974,4.7261615496\H,-2.7417732357,1.6039974241,3.7456442559\H,-1.4117648261,0.55604158

92,4.2498938024\H,-2.2485895668,0.928965306,0.7968907138\H,-0.2234515635,1.1967610
691,-0.4334720705\H,-3.6772770747,-0.2560649134,2.3366756219\H,-2.3725637343,-1.314
5478336,2.8463106605\Version=AM64L-G09RevC.01\State=2-A\HF=-349.3926796\

Sum of electronic and zero-point Energies= -349.219785
Sum of electronic and thermal Energies= -349.211308
Sum of electronic and thermal Enthalpies= -349.210364
Sum of electronic and thermal Free Energies= -349.253768

TRANSITION STATES

HEMA-HEMA-Gas

C,2.6368257402,-0.4209333121,-1.3513658919\C,2.2437516691,0.8771173717,-0.71015378
4\C,2.8960635095,2.1397814028,-1.1917477682\C,4.3825872263,2.1885615423,-0.8037532
252\C,1.8288955977,0.8742780127,0.6973959501\O,1.5568812262,-0.3566553929,1.159922
533\C,1.0603013586,-0.4645363311,2.5052527512\C,2.0890902256,-0.1034952691,3.57863
82081\O,1.959276099,1.2021461095,4.0830604435\O,1.7126764377,1.8864726979,1.37542
60024\C,0.1484580575,1.0561998046,-1.5186474177\C,-0.3517975667,2.2824716861,-1.18
73259531\C,-1.1159725617,2.4762604186,0.0651002135\O,-1.2719885773,1.3600025783,0.
790573423\C,-2.0734419041,1.4760686907,1.9837274072\C,-1.4632864093,2.3948302639,
3.0510399352\O,-2.1149760015,3.6372678331,3.1523895811\C,-0.1462302585,3.51864895
79,-2.0074551379\O,-1.5832953152,3.5536657824,0.3906250142\H,3.5776022196,-0.79064
09416,-0.921814935\H,2.7938872485,-0.2841578677,-2.4256265265\H,1.887874183,-1.199
8733692,-1.192843484\H,0.7704394181,-1.5140391011,2.5812824945\H,0.1763171469,0.17
10539534,2.6144418272\H,3.0962994043,-0.2932437505,3.1756575029\H,1.9472165194,-0.
769878912,4.4345337936\H,1.9700182331,1.808562974,3.3280946224\H,2.3814052565,2.9
998568459,-0.7560086629\H,2.7996875691,2.2014105416,-2.28291986\H,4.4953038474,2.1
462470413,0.2835878904\H,4.8372193631,3.1185953213,-1.1547073332\H,4.9370900785,1.
.3540649286,-1.2432815285\H,-0.163641118,0.1730258234,-0.9694479558\H,0.5695986424
,0.9044520195,-2.5094338403\H,0.3568343398,4.2959173784,-1.4226061292\H,-1.1098691
067,3.9388915298,-2.3135857398\H,0.4452886623,3.2995718083,-2.8989129914\H,-2.1505
746774,0.4442140606,2.3323785982\H,-3.0699988506,1.8407204332,1.7142582471\H,-0.38
87782778,2.5054102224,2.844166611\H,-1.56258154,1.9214713709,4.0322061991\H,-2.039

6521144,4.064934842,2.2876949155\\Version=AM64L-G09RevC.01\\State=2-A\\HF=-960.16
15648\\

Sum of electronic and zero-point Energies= -959.802838
Sum of electronic and thermal Energies= -959.780688
Sum of electronic and thermal Enthalpies= -959.779743
Sum of electronic and thermal Free Energies= -959.855373

ST-ST-Gas

C,-0.6069708315,-0.7508577191,3.3296177705\C,0.0061540586,-0.8076844982,2.06143963
11\C,1.1962043147,-1.5559981669,1.9387394336\C,1.7500727714,-2.2073961627,3.032683
6455\C,1.1323689365,-2.1346984583,4.2835746358\C,-0.0477696137,-1.4027384691,4.423
1575972\C,-0.5726924252,-0.1950877435,0.8866351174\C,-1.65712503,0.8396754085,0.97
36475205\C,-1.1350196938,2.1848726515,1.5035915005\C,-1.7103644285,-1.8978625869,-
0.0758058874\C,-0.8311393529,-2.9281164561,-0.2464448472\C,0.1313202404,-3.0495048
77,-1.3347611814\C,0.2555329409,-2.0851487912,-2.3524615287\C,1.2001356622,-2.22948
24388,-3.3617531061\C,2.049567139,-3.337049886,-3.3827245043\C,1.9446524845,-4.2993
513835,-2.3784049837\C,1.0007253003,-4.154613045,-1.3677790243\H,2.6686223813,-2.77
42963038,2.9127298348\H,-1.5259901671,-0.1866536203,3.4614728815\H,1.566671807,-2.
6414835313,5.1393846049\H,-0.5352787262,-1.3386851718,5.3914930649\H,0.925194455,-
4.9053792921,-0.5849280633\H,2.6014442956,-5.1639792188,-2.3824662231\H,-0.3928477
863,-1.2136365305,-2.3545612847\H,2.785976481,-3.4459658446,-4.1724829164\H,1.2773
152315,-1.4721272718,-4.1361864548\H,-0.7503345724,-3.6747202796,0.5410773079\H,-1.
9581110953,-1.2266155336,-0.8933392189\H,-2.4279152209,-1.9373158606,0.7382361855\H,
-1.9375762275,2.9276400177,1.5408403084\H,-0.3413737477,2.5716682795,0.85742275
48\H,-0.7205858,2.0732783169,2.5096772624\H,0.0980477896,-0.1135541436,0.031064735
6\H,1.676833405,-1.6220771954,0.9648375999\H,-2.0923632808,0.991057505,-0.02082292
72\H,-2.4739236946,0.4855433012,1.6151057587\\Version=AM64L-G09RevC.01\\State=2-
A\\HF=-658.9075181\\

Sum of electronic and zero-point Energies= -658.599067
Sum of electronic and thermal Energies= -658.583123
Sum of electronic and thermal Enthalpies= -658.582179
Sum of electronic and thermal Free Energies= -658.646093

ST-HEMA(R)-Gas

C,4.60328995,-1.5965572382,3.8519612089\C,4.6522156228,-2.7804795742,4.5804474516
\C,3.478444469,-3.3394817519,5.0867877404\C,2.2563914806,-2.7045303182,4.855547139
8\C,2.2078501335,-1.5175744576,4.1341384389\C,3.3833671127,-0.9371987243,3.6244207
702\C,3.3765232677,0.326227093,2.8909928913\C,2.415517194,1.2922432999,3.00813439
08\C,3.0370183662,2.7153694952,4.6351221897\C,3.9797730306,3.6146926336,3.8922052
642\C,3.6824375948,1.7055140767,5.4769745102\O,2.8300722917,1.0647376902,6.294465
9048\C,3.33976446,-0.0501818292,7.0532793298\C,4.3482186197,0.3401925109,8.1339879
552\O,5.692189382,0.1824134061,7.7519001884\C,1.6932672126,3.2605880867,5.0329305
355\C,1.8119080711,4.3342193836,6.1260067879\O,4.8719801002,1.4255452262,5.404438
8896\H,4.7641215345,3.0356243607,3.3989104177\H,4.4814928575,4.3073458614,4.58120
90515\H,3.4408502191,4.2118475862,3.1498012139\H,3.7860425759,-0.7822564822,6.371
8707436\H,2.4387042096,-0.4757207407,7.4992343562\H,4.2008725227,-0.3160065688,8.9
97433227\H,4.1317202086,1.3700354561,8.4607326803\H,5.7942676311,0.6179233321,6.8
918857176\H,1.0536955697,2.4497033057,5.3924717786\H,1.2125345132,3.695718333,4.1
47155098\H,0.8236705223,4.7103170848,6.4048316957\H,2.4130839631,5.1823152499,5.7
85225754\H,2.283028266,3.9182188605,7.0219400776\H,2.410850705,2.1341551786,2.322
2588732\H,1.4791977191,1.0817549945,3.5179943412\H,5.5206721491,-1.1498608334,3.4
782388305\H,5.6075131528,-3.2625974071,4.7618999288\H,1.2490220133,-1.0423472191,
3.9502001154\H,3.5150298246,-4.2640927744,5.6541850049\H,1.3375627855,-3.14038772
83,5.2362469152\H,4.2688266979,0.545028142,2.3075665918\Version=EM64L-G09RevB.
01\State=2-A\HF=-809.53717\

Sum of electronic and zero-point Energies= -809.203645

Sum of electronic and thermal Energies= -809.184657

Sum of electronic and thermal Enthalpies= -809.183713

Sum of electronic and thermal Free Energies= -809.252813

HEMA-ST(R)-Gas

C,0.6780869553,0.6125453988,-0.6958931116\H,1.4698248003,1.2610844095,-1.05412737
59\H,0.0169483211,1.0229232697,0.0628602829\C,0.774486287,-0.7436370735,-0.8391507
367\C,-0.1379819902,-1.7195736598,-0.1571673229\H,-0.7015985562,-2.3164823503,-0.88
27679531\H,-0.842484676,-1.1954048654,0.4925029189\H,0.437706295,-2.429256063,0.44

5770742\C,1.7695361488,-1.3325149732,-1.7479182139\O,1.9257398628,-2.5367460163,-1.8835334697\O,2.4908077577,-0.4256162212,-2.4311200294\C,3.4503723583,-0.9245119074,-3.380282229\H,3.7952764192,-0.0187260992,-3.88209764\H,2.9448031868,-1.5742120562,-4.1027797549\C,4.6256539007,-1.6749462334,-2.7487101498\H,4.76503648,-1.3020464064,-1.7218271749\H,5.5328205425,-1.4355242641,-3.3116589012\O,4.5043448498,-3.0742662009,-2.7904275996\H,3.6431720221,-3.2989249655,-2.4073586119\C,-0.6234364306,1.3976631711,-2.3509081162\H,0.9392238283,3.5390143813,-2.6841310662\C,0.0568542568,3.759663172,-2.0875936109\C,-2.2065824499,4.3204039015,-0.5694282011\C,-0.1383053754,5.0381336485,-1.5833493795\C,-0.8782623892,2.7299302124,-1.8493907014\C,-2.0142025018,3.0390146417,-1.0715371863\C,-1.2725508008,5.3270383562,-0.8211462941\H,0.5927658693,5.8150431997,-1.7854546837\H,-2.7526808797,2.2689876673,-0.8667695176\H,-1.4272434954,6.326691012,-0.4281318406\H,-3.0909201657,4.5380628113,0.0218594856\H,0.1798830158,1.3195079079,-3.082470955\C,-1.7005669368,0.3584584821,-2.4574982504\H,-1.2349860207,-0.6053678239,-2.6900565954\H,-2.2082119722,0.2282029974,-1.4927547956\H,-3.4878245033,-0.0812005061,-3.623239218\C,-2.7304810944,0.7039284176,-3.543915106\H,-3.2347329144,1.6489130292,-3.3222267204\H,-2.243286005,0.8067455984,-4.5181689167\\Version=AM64L-G09RevC.01\State=2-A\HF=-809.53317\

Sum of electronic and zero-point Energies=	-809.199612
Sum of electronic and thermal Energies=	-809.180463
Sum of electronic and thermal Enthalpies=	-809.179519
Sum of electronic and thermal Free Energies=	-809.250293