

## Supporting Information

# A Comprehensive Kinetic Study of the Conventional Free-Radical Polymerization of Seven-Membered Cyclic Ketene Acetals

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## Table of contents

1. Table S1. Polymerization of MDO and BMDO in bulk at different temperature.
2. Figure S1. SEC Chromatograms of P(MDO) prepared in bulk at 70°C and 120°C
3. Figure S2. SEC Chromatograms of P(BMDO) prepared in bulk at 70°C and 120°C
4. Figure S3. MDO bulk polymerization initiated at 70°C with various amount of AIBN.
5. Figure S4. MDO bulk polymerization initiated at 60°C with various amount of AIBN.
6. Figure S5. Evolution of  $M_n$  versus conversion for the bulk polymerization at 70°C of MDO initiated with various amount of AIBN.
7. Figure S6. Evolution of the dispersity versus conversion for the bulk polymerization at 70°C of MDO initiated with various amount of AIBN.
8. Table S2. copolymerization of MDO and BMDO (1:1) in bulk at different temperature

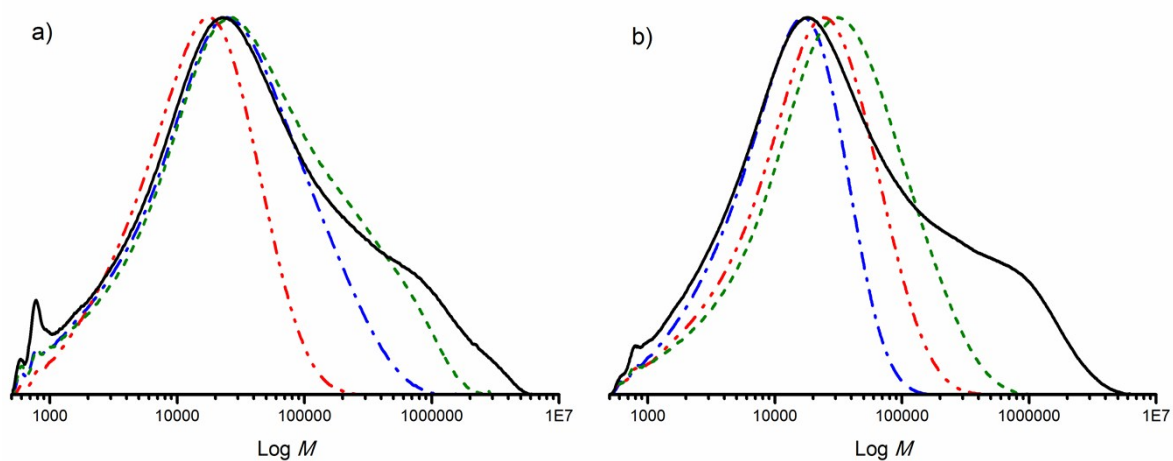
9. Figure S7. SEC Chromatograms of P(MDO-*co*-BMDO) prepared in bulk at 70°C and 120°C
  
10. Figure S8. <sup>1</sup>H and <sup>13</sup>C NMR spectra of P(MeBMDO)
  
11. Table S3. Kinetic rate constants used for the PREDICI modelings of the bulk polymerization of MDO and BMDO.
  
12. Table S4. Kinetic rate constants used for the PREDICI modelings of the bulk polymerization of Me BMDO.
  
13. PREDICI modelings: discussion about the kinetic rate constants
  
14. DFT Calculations

**Table S1.** Polymerization of MDO and BMDO in bulk at different temperature. ( $[CKA]_0 : [Initiator]_0 = 100:3$ ).

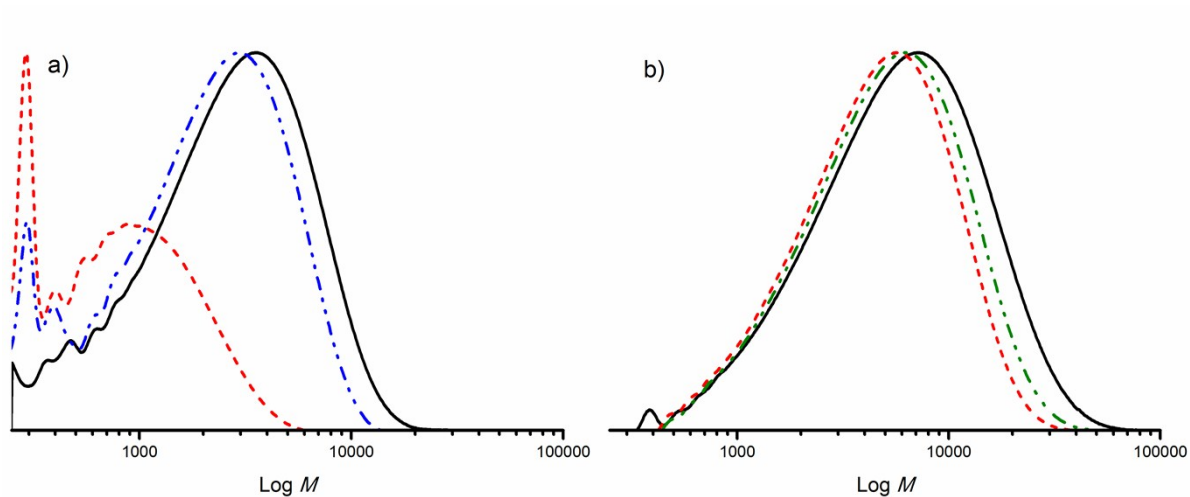
Monomer	Initiator	Temperature (°C)	Time (h)	Conversion	$M_n$ (g.mol <sup>-1</sup> )	$M_w$ (g.mol <sup>-1</sup> )	$\bar{D}$
<b>MDO</b>	AIBN	70	1	0.41	7300	21400	2.9
	AIBN	70	3	0.69	8800	55600	6.3
	AIBN	70	6	0.83	10300	118100	11.4
	AIBN	70	12	0.86	8900 <sup>a</sup>	197700	22.2
	AIBN	50	24	0.55	8400	35200	4.2
	DTBP	120	1	0.38	6600	17500	2.6
	DTBP	120	3	0.69	8700	31300	3.6
	DTBP	120	6	0.89	10800	55200	5.1
	DTBP	150	1	0.97	9400	186700	19.8
	VAm-111	120	3	0.88	10400	42400	4.0
<b>BMDO</b>	AIBN	70	3	0.055	1000	1300	1.3
	AIBN	70	6	0.094	1500	2900	1.9
	AIBN	70	24	0.188	2000	3700	3.4
	DTBP	120	3	0.013	-	-	-
	DTBP	120	6	0.026	-	-	-
	DTBP	120	24	0.029	-	-	-
	DTBP	150	1	-	800	1100	1.4
	VAm-111	120	1,5	0.15	3500	6000	1.7
	VAm-111	120	3	0.28	3100	5800	1.8
	VAm-111	120	6	0.37	3400	6700	1.9
	VAm-111	120	15	0.47	3600	8100	2.2
	VAm-111	120	24	0.48	3700	7700	2.1

*a : partially insoluble*

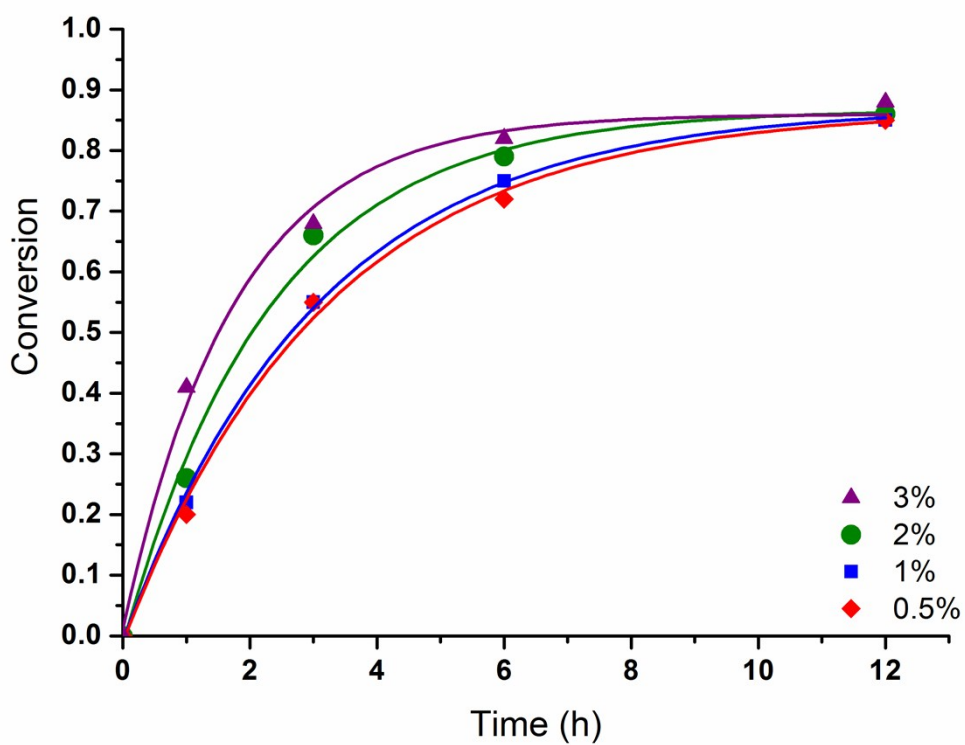
**Figure S1.** SEC Chromatograms of P(MDO) prepared in bulk at a) 70°C at conversions of 0.41 (—•—•—), 0.69 (—•—•—), 0.83 (—•—•—) and 0.86 (—); and b) 120°C at conversions of 0.38 (—•—•—), 0.69 (—•—•—), 0.89 (—•—•—) and also at 150°C 0.97 (—)



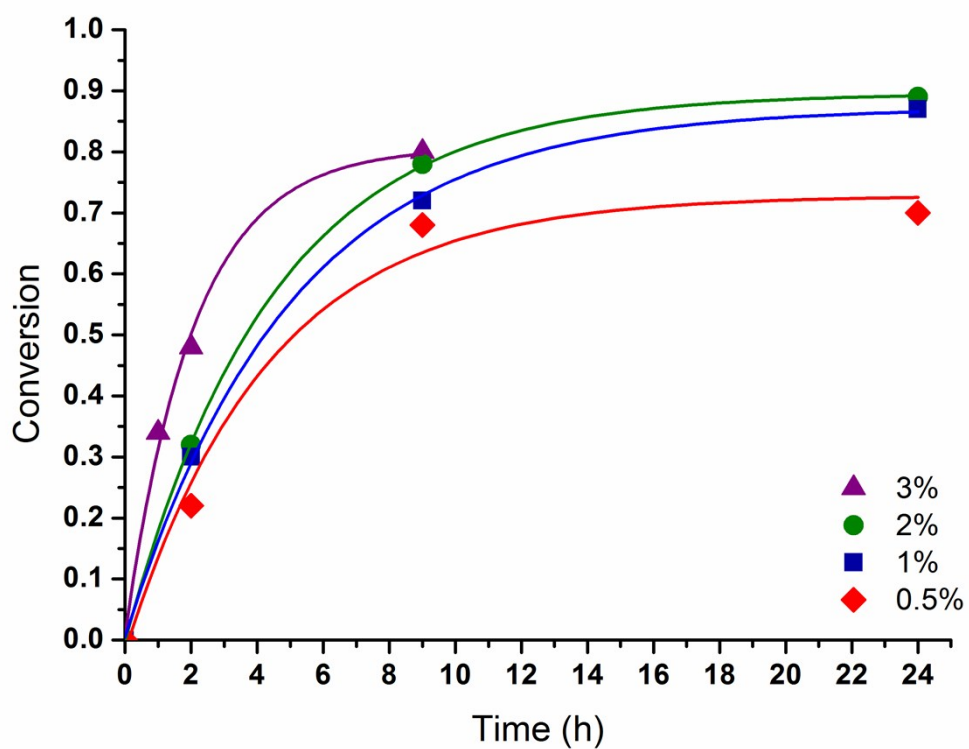
**Figure S2.** SEC Chromatograms of P(BMDO) prepared in bulk at a) 70°C at conversions of 0.05 (- - -), 0.10 (-·-·-·-), 0.19 (-); and b) 120°C at conversions of 0.28 (- - -), 0.37 (-·-·-·-) and 0.48 (-).



**Figure S3.** MDO bulk polymerization initiated at 70°C with various amount of AIBN.

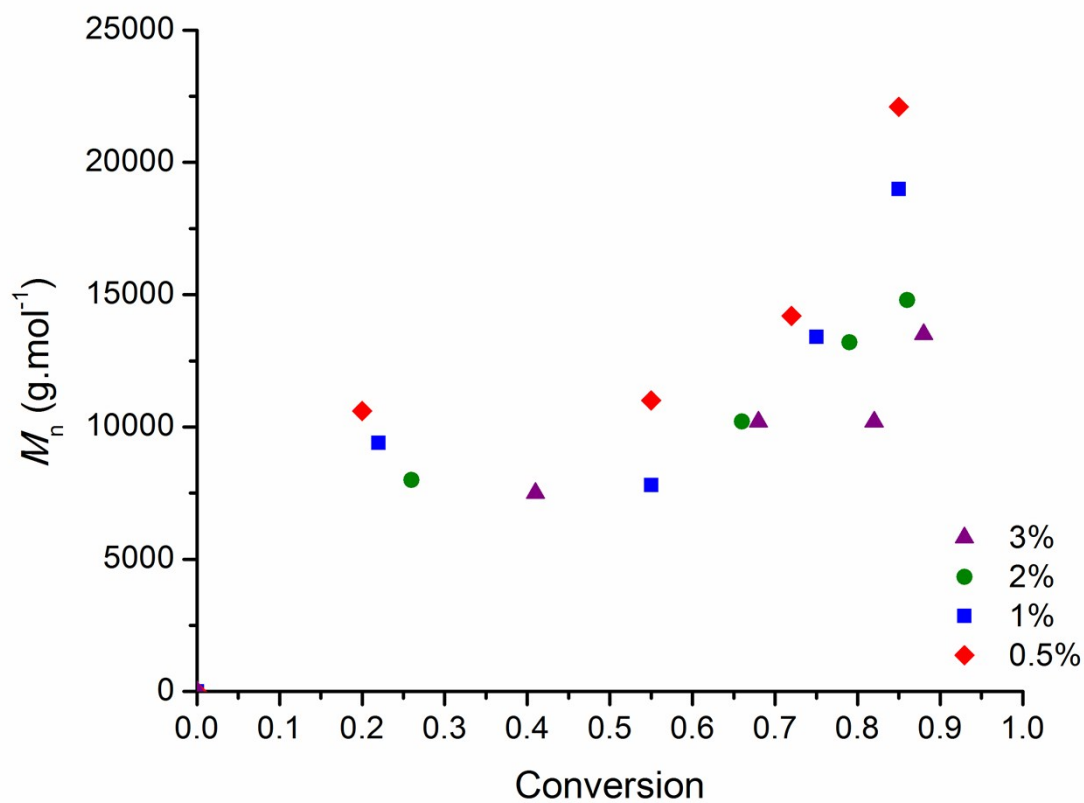


**Figure S4.** MDO bulk polymerization initiated at 60°C with various amount of AIBN.

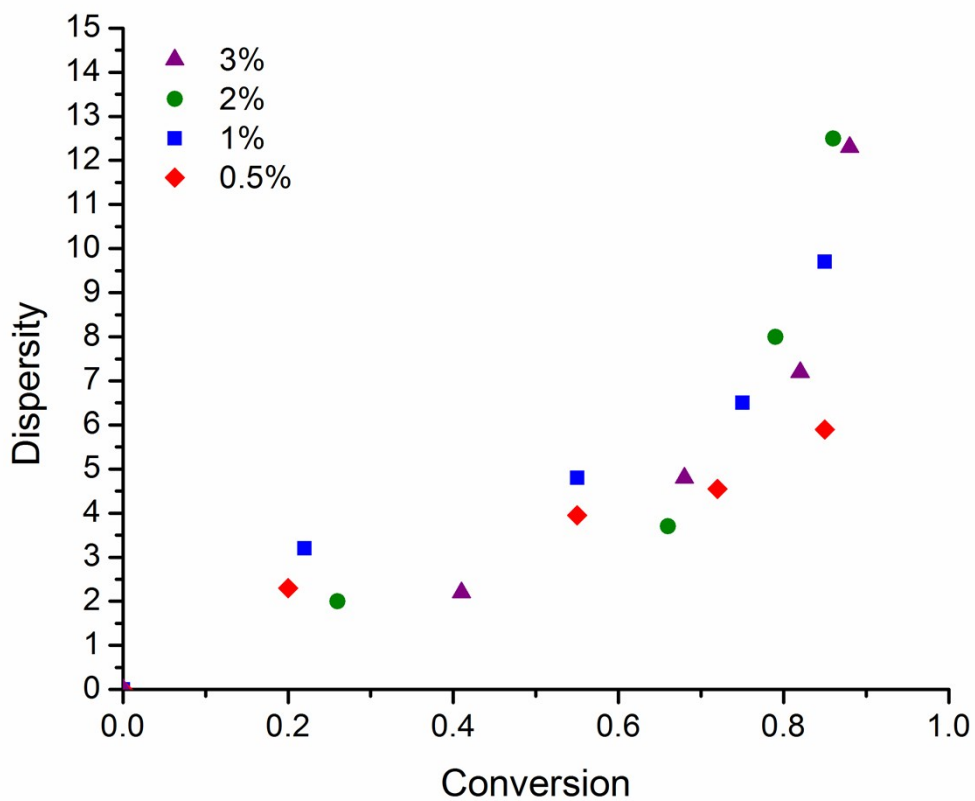




**Figure S5.** Evolution of  $M_n$  versus conversion for the bulk polymerization at 70°C of MDO initiated with various amount of AIBN.



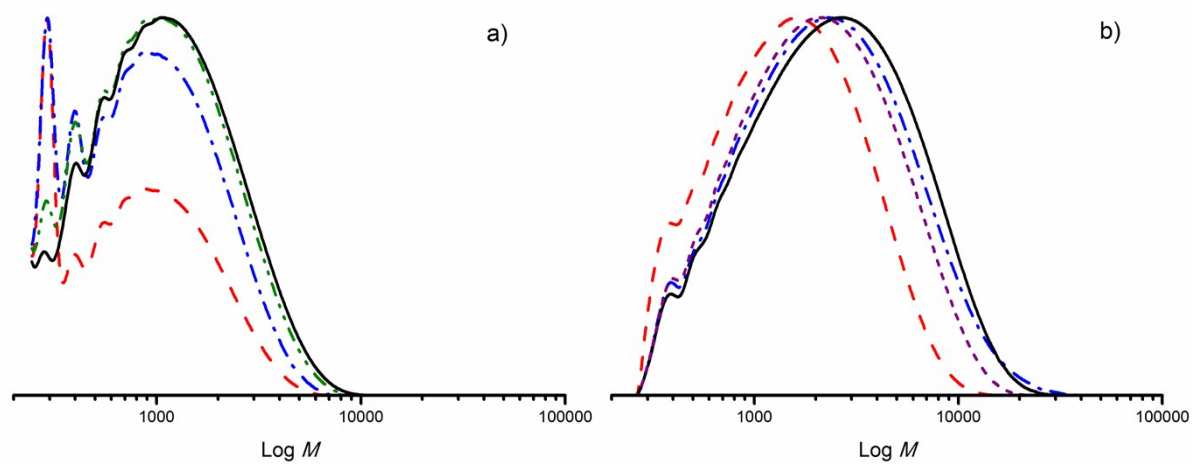
**Figure S6.** Evolution of the dispersity versus conversion for the bulk polymerization at 70°C of MDO initiated with various amount of AIBN.



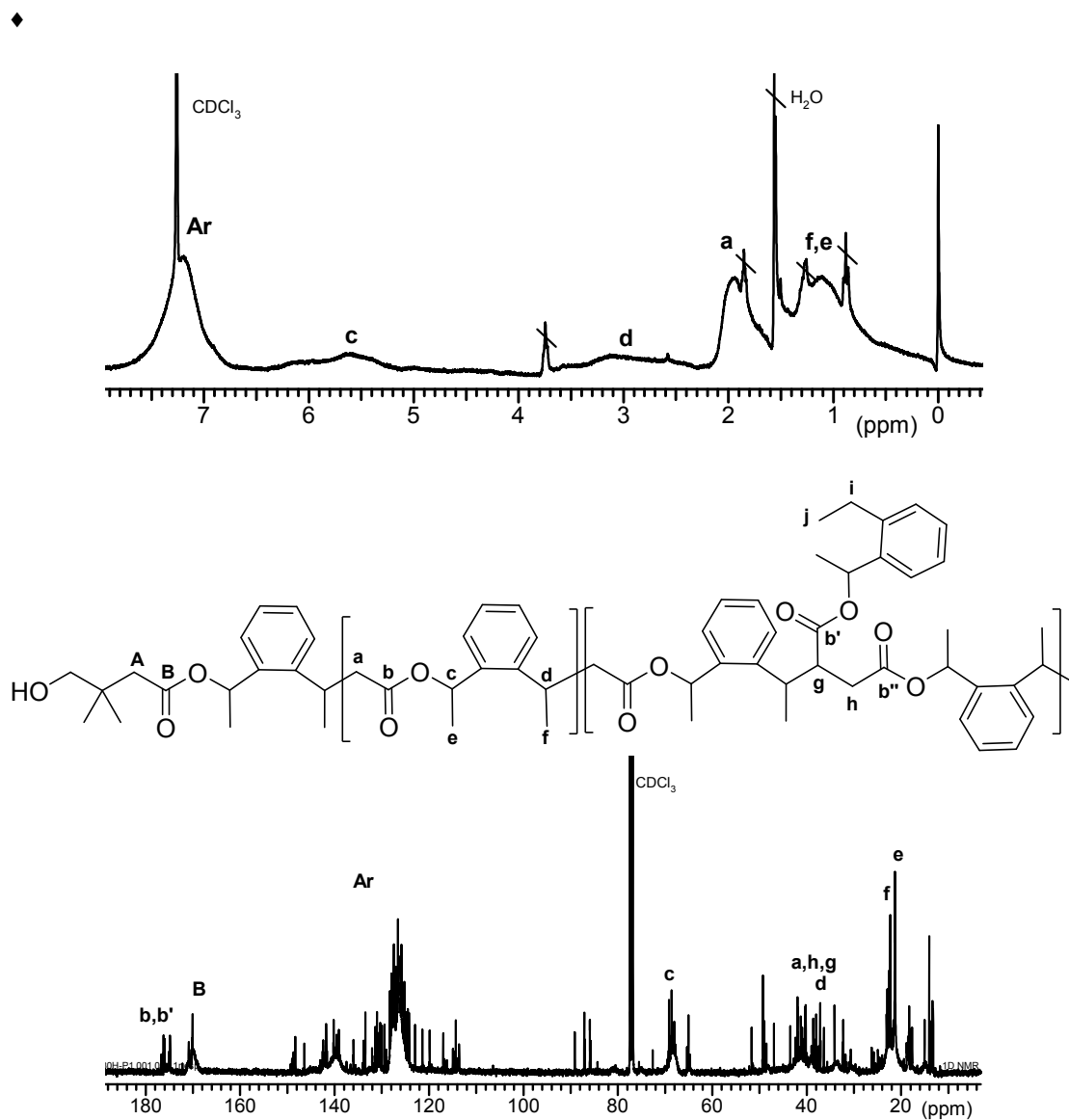
**Table S2.** Copolymerization of MDO and BMDO (1:1) in bulk at different temperature. ( $[MDO]_0 : [BMDO]_0 : [Initiator]_0 = 50:50:3$ ).

Initiator	Temperature (°C)	Time (h)	Conversion	$M_n$ (g.mol <sup>-1</sup> )	$M_w$ (g.mol <sup>-1</sup> )	$D$
AIBN	70	3	0.06	700	1200	1.6
		6	0.12	800	1200	1.6
		15	0.21	900	1400	1.5
		24	0.27	1000	1500	1.5
DTBP	120	6	0.19	1100	1900	1.8
		15	0.50	1500	3600	2.2
		24	0.56	1600	3400	2.2
	150	1	0.41	1400	2800	2.0

**Figure S7.** SEC Chromatograms of P(MDO-*co*-BMDO) prepared in bulk at a) 70°C at conversions of 0.06 (---), 0.12 (-·-·-), 0.21 and (-·-·-) 0.27 (—); and b) 120°C at conversions of 0.19 (---), 0.41 (- - -), 0.50 (-·-·-) and 0.56 (—).



**Figure S8.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of P(MeBMDO).



**Table S3.** Kinetic rate constants used for the PREDICI modeling of the bulk polymerization of MDO and BMDO.

Rate Constant	Unit	70°C, AIBN		120°C, VAm-111	
		MDO	BMDO	MDO	BMDO
$k_{d,amorç}$	s <sup>-1</sup>	3.20 × 10 <sup>-5</sup>		1.00 × 10 <sup>-4</sup>	
$k_{dim}$	L.mol <sup>-1</sup> .s <sup>-1</sup>	2.00 × 10 <sup>9</sup>			
$k_{add}$	L.mol <sup>-1</sup> .s <sup>-1</sup>	1.90 × 10 <sup>1</sup>		3.70 × 10 <sup>2</sup>	
$k_p$	L.mol <sup>-1</sup> .s <sup>-1</sup>	2.43 × 10 <sup>3</sup>	2.25 × 10 <sup>1</sup>	8.43 × 10 <sup>3</sup>	1.42 × 10 <sup>2</sup>
$k_t$	L.mol <sup>-1</sup> .s <sup>-1</sup>	1.0 × 10 <sup>9</sup>	4.0 × 10 <sup>8</sup>	1.0 × 10 <sup>9</sup>	4.0 × 10 <sup>8</sup>
[CKA]	mol.L <sup>-1</sup>	8.5	7.5	8.5	7.5
<i>simulated</i> $M_n$	g.mol <sup>-1</sup>	27000-48000	750-1100	30000-75000	2000-2800
<i>simulated</i> $M_w$	g.mol <sup>-1</sup>	62000-95000	1400-2200	80000-150000	3800-8800

**Table S4.** Kinetic rate constants used for the PREDICI modeling of the bulk polymerization of Me BMDO.

Rate Constant.	Unit	120°C VAm-111	160°C ABIB
$k_{d,amorç}$	s <sup>-1</sup>	$1.00 \times 10^{-4}$	$1.60 \times 10^{-5}$
$k_{dim}$	L.mol <sup>-1</sup> .s <sup>-1</sup>	$2.00 \times 10^9$	$2.00 \times 10^9$
$k_{add}$	L.mol <sup>-1</sup> .s <sup>-1</sup>	$3,70 \times 10^2$	$4.0 \times 10^2$
$k_p$	L.mol <sup>-1</sup> .s <sup>-1</sup>	$2.6 \times 10^0$	$1.09 \times 10^1$
$k_t$	L.mol <sup>-1</sup> .s <sup>-1</sup>		$1.00 \times 10^7$
[CKA]	mol.L <sup>-1</sup>		7.5
<i>simulated</i> $M_n$	g.mol <sup>-1</sup>	500	2400
<i>simulated</i> $M_w$	g.mol <sup>-1</sup>	1200	4800

### 13. PREDICI modelings: discussion about the kinetic rate constants

To perform the PREDICI modelings, many kinetic rate constants are necessary and very few data are available for CKA monomers. The dissociation of VAm-111 is not well described; *i.e.* only the temperature that lead to 10 hours of half-life is described (111°C) as well as an indication of the activation energy (132 kJ.mol<sup>-1</sup>).<sup>1</sup> Besides these values are determined in ethyl-benzene. This leads to  $k_{dVAM} = 5 \cdot 10^{-5} \text{ s}^{-1}$  at 120°C. A value of  $1.0 \times 10^{-4} \text{ s}^{-1}$  that is a two fold increase of the value to take into account the polar medium seems reasonable. The  $k_{dim}$  value is classical for such kind of radicals.<sup>2</sup>

An average efficiency of 50 % was used to take the cage effect into account for the whole polymerization process ( $[VAm-111]_0 = 1.15 \cdot 10^{-1} \text{ mol.L}^{-1}$  for 3 mol% of initiator initially). The termination rate constant  $k_t$  for the BMDO was set to  $4.0 \cdot 10^8 \text{ L.mol}^{-1}.\text{s}^{-1}$  and a higher value of  $1.0 \cdot 10^9 \text{ L.mol}^{-1}.\text{s}^{-1}$  was selected for the non-stabilized primary radical PMDO. In case of MeBMDO, the  $k_t$  was set to  $1.0 \cdot 10^7 \text{ L.mol}^{-1}.\text{s}^{-1}$  since the propagating radical is similar to the polystyrene macroradical but with a chain that is less flexible due to the presence of the extra methyl moieties onto the backbone.

The addition of alkyl radicals to the CKA function seemed to be independent of the nature of the CKA but more to the nature of the alkyl radical. There is no information on the rate of addition of radicals derivated from both AIBN and VAm-111 onto CKA monomers. We thus calculated the addition of the radicals 2-cyano-2-propyl (PCN) and 2-methylcarbonyl-2-propyl (Pest) onto BMDO using the B3LYP/6-31G(d) level of theory. ( $\Delta H^\ddagger = 38.1 \text{ kJ.mol}^{-1}$  for PEst and  $41.68 \text{ kJ.mol}^{-1}$  for PCN). The kinetic rate constants were then calculated using the Arrhenius equation  $k = A \cdot e^{-E_a/RT}$  with  $E_a = \Delta H^\ddagger + 2RT$ .

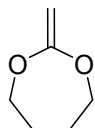


The concentration of BMDO was already determined at  $7.5 \text{ mol.L}^{-1}$ .<sup>3</sup> A similar study with MDO led to a concentration of  $8.5 \text{ mol.L}^{-1}$ . The concentration for MeBMDO was considered similar to the one of BMDO.

## 14. DFT Calculations.

### *Monomers*

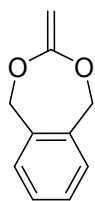
#### MDO



#### AT\_AC77\_1

Zero-point correction= 0.150015 (Hartree/Particle)  
Thermal correction to Energy= 0.157562  
Thermal correction to Enthalpy= 0.158506  
Thermal correction to Gibbs Free Energy= 0.118345  
Sum of electronic and zero-point Energies= -384.919665  
Sum of electronic and thermal Energies= -384.912118  
Sum of electronic and thermal Enthalpies= -384.911174  
Sum of electronic and thermal Free Energies= -384.951335

Tag	Symbol	X	Y	Z
1	C	2.6470740	-0.0000830	-0.0001530
2	C	1.3120230	0.0000320	0.0000350
3	H	3.1908130	-0.9068400	0.2302560
4	H	3.1909180	0.9065800	-0.2306920
5	O	0.5963660	-1.0764080	0.4365860
6	O	0.5964500	1.0766250	-0.4362940
7	C	-0.5529580	-1.4607180	-0.3440530
8	C	-0.5530750	1.4606830	0.3441420
9	C	-1.8186750	-0.7542200	0.1370680
10	H	-0.3633910	-1.2705160	-1.4077510
11	H	-0.6408910	-2.5412190	-0.1979160
12	C	-1.8186480	0.7541200	-0.1372900
13	H	-0.3637190	1.2704040	1.4078630
14	H	-0.6411110	2.5411850	0.1980870
15	H	-1.9178850	-0.9409940	1.2145200
16	H	-2.6870000	-1.2203400	-0.3475450
17	H	-1.9176030	0.9408930	-1.2147660
18	H	-2.6870960	1.2202300	0.3471110

**BMDO**

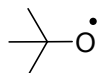
AT\_A0mon

Zero-point correction= 0.172400 (Hartree/Particle)  
 Thermal correction to Energy= 0.182180  
 Thermal correction to Enthalpy= 0.183124  
 Thermal correction to Gibbs Free Energy= 0.137190  
 Sum of electronic and zero-point Energies= -537.318730  
 Sum of electronic and thermal Energies= -537.308950  
 Sum of electronic and thermal Enthalpies= -537.308006  
 Sum of electronic and thermal Free Energies= -537.353940

Tag	Symbol	X	Y	Z
1	C	-0.5745110	-1.4960430	-0.1819560
2	C	-2.3938610	0.0000110	0.0001070
3	C	-0.5745230	1.4960450	0.1816980
4	H	-0.8915820	-1.5629040	-1.2312580
5	H	-0.4169060	-2.5140010	0.1848310
6	H	-0.4166570	2.5138770	-0.1853340
7	O	-1.6621860	-0.9798870	0.6064510
8	C	0.7081430	0.7001770	0.0578710
9	C	0.7082330	-0.7003520	-0.0580140
10	C	1.9296190	-1.3808770	-0.1103580
11	C	3.1424000	-0.6948530	-0.0565090
12	C	3.1423230	0.6949590	0.0566470
13	C	1.9294610	1.3808410	0.1103390
14	H	4.0791750	1.2436150	0.0987580
15	H	4.0793090	-1.2434220	-0.0985120
16	H	1.9287970	-2.4658440	-0.1928440
17	H	1.9285090	2.4658100	0.1927880
18	O	-1.6624790	0.9801110	-0.6063310
19	H	-0.8913450	1.5632710	1.2310620
20	C	-3.7271610	-0.0001940	0.0000500
21	H	-4.2714930	0.8517950	-0.3858240
22	H	-4.2712120	-0.8522740	0.3861140

## H-abstractions

tBuO<sup>•</sup>

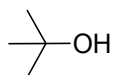


AT\_\_TBO

Zero-point correction= 0.118157 (Hartree/Particle)  
Thermal correction to Energy= 0.124876  
Thermal correction to Enthalpy= 0.125820  
Thermal correction to Gibbs Free Energy= 0.088449  
Sum of electronic and zero-point Energies= -232.888015  
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Sum of electronic and thermal Enthalpies= -232.880352  
Sum of electronic and thermal Free Energies= -232.917723

Tag	Symbol	X	Y	Z
1	C	-0.0000390	-0.0263210	0.0811510
2	C	0.0010060	1.3892660	-0.5779100
3	H	0.0002740	1.2632720	-1.6660850
4	H	-0.8888910	1.9508560	-0.2814990
5	H	0.8923210	1.9491750	-0.2825420
6	C	-1.2784590	-0.7911660	-0.3161400
7	H	-1.3071330	-1.7628630	0.1888010
8	H	-2.1661310	-0.2246770	-0.0182450
9	H	-1.3161370	-0.9671300	-1.3973170
10	C	1.2772140	-0.7930910	-0.3162720
11	H	2.1655590	-0.2281160	-0.0175220
12	H	1.3040970	-1.7652180	0.1879370
13	H	1.3151840	-0.9683650	-1.3975470
14	O	0.0003150	0.2601170	1.4323810

tBuOH

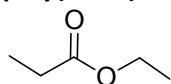


AT\_B\_TBO+H

Zero-point correction= 0.130779 (Hartree/Particle)  
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Thermal correction to Enthalpy= 0.138656  
Thermal correction to Gibbs Free Energy= 0.101619  
Sum of electronic and zero-point Energies= -233.540179  
Sum of electronic and thermal Energies= -233.533246  
Sum of electronic and thermal Enthalpies= -233.532302  
Sum of electronic and thermal Free Energies= -233.569340

Tag	Symbol	X	Y	Z
1	C	-0.0054160	-0.0004250	0.0138040
2	C	0.6618830	1.2810030	-0.5091670
3	H	0.6236160	1.3370820	-1.6033900
4	H	0.1607470	2.1632780	-0.0976140
5	H	1.7185110	1.3189060	-0.2122690
6	C	-1.4903010	-0.0319190	-0.3560670
7	H	-1.9640980	-0.9297980	0.0541280
8	H	-2.0022130	0.8427650	0.0582750
9	H	-1.6228570	-0.0325410	-1.4432800
10	C	0.7179880	-1.2495390	-0.5118290
11	H	1.7755220	-1.2404380	-0.2156410
12	H	0.2577160	-2.1544690	-0.1016750
13	H	0.6818280	-1.3054670	-1.6060790
14	O	0.0150590	-0.0016960	1.4524600
15	H	0.9458300	0.0195300	1.7274200

**poly(MDO)**

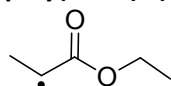


AT\_R-Ester

Zero-point correction= 0.141786 (Hartree/Particle)  
Thermal correction to Energy= 0.150652  
Thermal correction to Enthalpy= 0.151597  
Thermal correction to Gibbs Free Energy= 0.107355  
Sum of electronic and zero-point Energies= -346.880352  
Sum of electronic and thermal Energies= -346.871485  
Sum of electronic and thermal Enthalpies= -346.870541  
Sum of electronic and thermal Free Energies= -346.914783

Tag	Symbol	X	Y	Z
1	C	-3.0875230	-0.4567180	-0.0020060
2	C	-1.8575120	0.4316630	0.0000730
3	C	0.5033440	0.1905130	0.0014500
4	H	-3.1063870	-1.0969360	-0.8898990
5	H	-1.8181100	1.0773900	0.8834560
6	H	-3.9925920	0.1605600	-0.0027180
7	H	-1.8160670	1.0787620	-0.8821870
8	C	1.6356900	-0.8198120	0.0032080
9	H	1.4995910	-1.4761350	-0.8660440
10	H	1.5045600	-1.4666040	0.8804360
11	C	3.0147450	-0.1634230	-0.0038320
12	H	3.1494990	0.4758630	0.8736830
13	H	3.8008700	-0.9255620	-0.0011870
14	H	3.1455970	0.4654640	-0.8894600
15	O	-0.6978220	-0.4317960	0.0007630
16	O	0.6339680	1.3957970	0.0011870
17	H	-3.1085930	-1.0981380	0.8849650

poly(MDO)<sup>o</sup> (a)

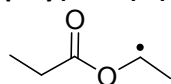


AT\_R-Ester-H1

Zero-point correction= 0.127580 (Hartree/Particle)  
Thermal correction to Energy= 0.136696  
Thermal correction to Enthalpy= 0.137640  
Thermal correction to Gibbs Free Energy= 0.092519  
Sum of electronic and zero-point Energies= -346.231181  
Sum of electronic and thermal Energies= -346.222066  
Sum of electronic and thermal Enthalpies= -346.221121  
Sum of electronic and thermal Free Energies= -346.266243

Tag	Symbol	X	Y	Z
1	C	-3.1430660	-0.3775220	0.0940530
2	C	-1.8766620	0.3632010	-0.1220670
3	C	0.4827590	0.2117730	-0.0281990
4	H	-3.2042310	-1.2620650	-0.5528500
5	H	-3.9974790	0.2701860	-0.1262980
6	C	1.5978760	-0.8117290	-0.0370470
7	H	1.5015680	-1.4014240	-0.9585080
8	H	1.4145910	-1.5193270	0.7818630
9	C	2.9822480	-0.1756700	0.0722800
10	H	3.0811860	0.3930500	1.0017380
11	H	3.7585450	-0.9473630	0.0551120
12	H	3.1626650	0.5157480	-0.7559640
13	O	-0.7367090	-0.4129380	-0.0759720
14	O	0.6135130	1.4133890	0.0110220
15	H	-3.2544320	-0.7326840	1.1335220
16	H	-1.7357700	1.4199500	0.0668550

poly(MDO)<sup>o</sup> (b)

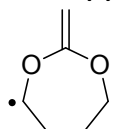


AT\_R-Ester-H2

Zero-point correction= 0.128508 (Hartree/Particle)  
Thermal correction to Energy= 0.137346  
Thermal correction to Enthalpy= 0.138290  
Thermal correction to Gibbs Free Energy= 0.094106  
Sum of electronic and zero-point Energies= -346.238882  
Sum of electronic and thermal Energies= -346.230044  
Sum of electronic and thermal Enthalpies= -346.229100  
Sum of electronic and thermal Free Energies= -346.273284

Tag	Symbol	X	Y	Z
1	C	-3.0524020	-0.4829140	0.0001040
2	C	-1.8254910	0.4102280	-0.0000870
3	C	0.5366540	0.1940000	-0.0000140
4	H	-3.0695410	-1.1239420	-0.8872830
5	H	-3.9601130	0.1304630	0.0001990
6	C	1.6418780	-0.7450820	-0.0000210
7	C	3.0521860	-0.2815770	0.0000190
8	H	3.0973930	0.8099570	-0.0002690
9	H	3.5946170	-0.6603110	0.8791710
10	H	3.5948640	-0.6607430	-0.8787870
11	O	-0.6654920	-0.4453760	-0.0001270
12	O	0.6489040	1.4139600	0.0000690
13	H	-3.0693050	-1.1238470	0.8875620
14	H	-1.7901100	1.0587710	0.8821440
15	H	-1.7903010	1.0586120	-0.8824360
16	H	1.4082390	-1.8055640	0.0001640



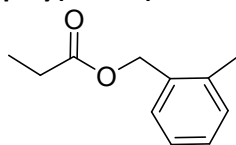
**MDO° (c)**

## AT\_B\_C7-H

Zero-point correction= 0.136278 (Hartree/Particle)  
 Thermal correction to Energy= 0.144016  
 Thermal correction to Enthalpy= 0.144960  
 Thermal correction to Gibbs Free Energy= 0.103660  
 Sum of electronic and zero-point Energies= -384.268523  
 Sum of electronic and thermal Energies= -384.260786  
 Sum of electronic and thermal Enthalpies= -384.259841  
 Sum of electronic and thermal Free Energies= -384.301141

Tag	Symbol	X	Y	Z
1	C	-2.4401110	-0.1893790	0.4540170
2	C	-1.2408410	0.0171230	-0.0977470
3	H	-2.8617220	-1.1857350	0.4655820
4	H	-3.0120490	0.6362300	0.8580570
5	O	-0.5092720	-0.9750180	-0.6714350
6	O	-0.7462350	1.2946110	-0.1988030
7	C	0.5637160	-1.5326260	0.1146950
8	C	0.6026730	1.5362020	-0.3149340
9	C	1.8282310	-0.6931920	0.0018050
10	H	0.2308300	-1.6195790	1.1580590
11	H	0.7192650	-2.5386310	-0.2851190
12	C	1.6093180	0.7580980	0.4729480
13	H	0.7642390	2.5855360	-0.5351920
14	H	2.1625960	-0.6914860	-1.0423320
15	H	2.6184780	-1.1636630	0.6024010
16	H	1.3246030	0.7426340	1.5419460
17	H	2.5598980	1.3005960	0.4138010

**poly(BMDO)**

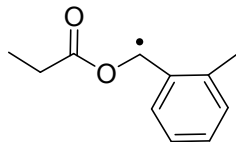


AT\_R0ouvMe

Zero-point correction= 0.219850 (Hartree/Particle)  
Thermal correction to Energy= 0.233295  
Thermal correction to Enthalpy= 0.234239  
Thermal correction to Gibbs Free Energy= 0.178275  
Sum of electronic and zero-point Energies= -577.853475  
Sum of electronic and thermal Energies= -577.840031  
Sum of electronic and thermal Enthalpies= -577.839086  
Sum of electronic and thermal Free Energies= -577.895050

Tag	Symbol	X	Y	Z
1	C	-0.0868490	0.5538640	1.3856470
2	C	-2.0941350	-0.0353670	0.2279190
3	C	1.6850350	2.3589590	-0.1844560
4	H	-0.4472960	-0.1799520	2.1083090
5	H	0.1691950	1.4794090	1.9059680
6	H	2.3550480	2.8400680	-0.9034420
7	O	-1.1957640	0.9355600	0.5219260
8	C	1.9195340	0.8652470	-0.1444880
9	C	1.0803270	0.0081720	0.5993980
10	C	1.3250070	-1.3694780	0.6077480
11	C	2.3969930	-1.9136570	-0.1000270
12	C	3.2322450	-1.0712450	-0.8312980
13	C	2.9882440	0.3032290	-0.8512970
14	H	4.0711070	-1.4794110	-1.3892010
15	H	2.5732410	-2.9856670	-0.0824260
16	H	0.6547520	-2.0173750	1.1655870
17	H	3.6407740	0.9557350	-1.4271760
18	O	-2.0476580	-1.1616710	0.6738600
19	H	1.8667120	2.8244590	0.7939410
20	C	-4.2562270	-0.5306910	-1.0026780
21	H	-4.9903810	-0.1172080	-1.7019090
22	H	-3.8426900	-1.4463870	-1.4349440
23	H	-4.7764520	-0.8092600	-0.0812070
24	C	-3.1533280	0.4884340	-0.7236680
25	H	-2.6432670	0.7860630	-1.6494830
26	H	-3.5583100	1.4164970	-0.3011840
27	H	0.6538670	2.5970980	-0.4659160

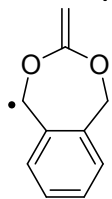
poly(BMDO)<sup>o</sup> (a)



AT\_R0ouvMe-H

Zero-point correction= 0.206151 (Hartree/Particle)  
Thermal correction to Energy= 0.219678  
Thermal correction to Enthalpy= 0.220623  
Thermal correction to Gibbs Free Energy= 0.164046  
Sum of electronic and zero-point Energies= -577.221313  
Sum of electronic and thermal Energies= -577.207786  
Sum of electronic and thermal Enthalpies= -577.206842  
Sum of electronic and thermal Free Energies= -577.263418

Tag	Symbol	X	Y	Z
1	C	-0.0909210	-0.8237310	-0.0008770
2	C	-2.4115770	-0.4028380	-0.0012300
3	C	0.8314590	2.1312130	-0.0002750
4	H	1.4201300	3.0540550	-0.0006000
5	O	-1.1229400	0.0803920	-0.0009880
6	C	1.7473330	0.9300640	-0.0000630
7	C	1.2584310	-0.4227110	-0.0002960
8	C	2.2149590	-1.4845250	0.0001450
9	C	3.5761070	-1.2420080	0.0007850
10	C	4.0459690	0.0771870	0.0009760
11	C	3.1265400	1.1315800	0.0005750
12	H	5.1121670	0.2844060	0.0014640
13	H	4.2742150	-2.0747860	0.0010990
14	H	1.8480400	-2.5080950	-0.0000570
15	H	3.4962700	2.1546430	0.0007460
16	O	-2.6774660	-1.5811770	-0.0007890
17	H	0.1762930	2.1474850	0.8778840
18	C	-4.8497330	0.2721140	0.0041180
19	H	-5.5283970	1.1308860	0.0017630
20	H	-5.0666680	-0.3427870	-0.8742390
21	H	-5.0615640	-0.3337360	0.8900130
22	C	-3.3970720	0.7443090	-0.0025820
23	H	-3.1827170	1.3692430	-0.8795900
24	H	-3.1767440	1.3771650	0.8671320
25	H	0.1759220	2.1469960	-0.8781470
26	H	-0.3926670	-1.8631200	-0.0009080


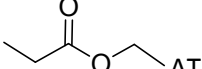
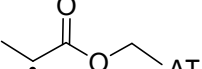


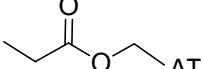
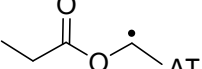


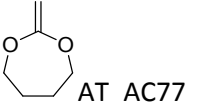
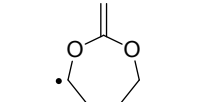


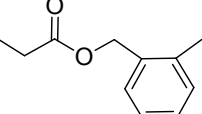
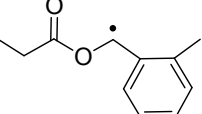


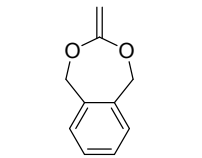
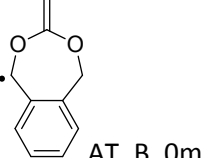

**BMDO° (c)**

AT\_B\_0mon-H

Zero-point correction= 0.158859 (Hartree/Particle)  
 Thermal correction to Energy= 0.168836  
 Thermal correction to Enthalpy= 0.169780  
 Thermal correction to Gibbs Free Energy= 0.122487  
 Sum of electronic and zero-point Energies= -536.688020  
 Sum of electronic and thermal Energies= -536.678043  
 Sum of electronic and thermal Enthalpies= -536.677098  
 Sum of electronic and thermal Free Energies= -536.724391

Tag	Symbol	X	Y	Z
1	C	0.5894430	-1.4461620	0.3635240
2	C	2.3930660	0.0078200	-0.1265770
3	C	0.4827050	1.5213790	0.0977390
4	H	0.9783700	-1.3333680	1.3849900
5	H	0.4629770	-2.5138620	0.1665500
6	H	0.3927760	2.6016750	0.0999700
7	O	1.6044720	-0.9949470	-0.5664200
8	C	-0.6757710	0.7203160	0.0552040
9	C	-0.6988540	-0.7055130	0.1617040
10	C	-1.9080110	-1.3869550	0.0905060
11	C	-3.1225480	-0.7097640	-0.0651140
12	C	-3.1176530	0.6892190	-0.1629690
13	C	-1.9259180	1.3901080	-0.1072870
14	H	-4.0525280	1.2291820	-0.2873400
15	H	-4.0548280	-1.2637390	-0.1175130
16	H	-1.9033100	-2.4728800	0.1590990
17	H	-1.9297370	2.4743070	-0.1883760
18	O	1.7843450	1.1675560	0.2970900
19	C	3.7266920	-0.0654580	-0.1109290
20	H	4.3233400	0.7990990	0.1483900
21	H	4.2134880	-0.9912180	-0.3859350

$$\text{Enthalpy of reaction } \Delta H_r = H_{(t\text{BuOH} + R^\circ)} - H_{(t\text{BuO}^\circ + R\text{-H})}$$

		Sum of electronic and thermal Enthalpies				$\Delta H_r$
		Hartree				
		tBuO <sup>°</sup>	R-H	R <sup>°</sup>	tBuOH	kJ.mol <sup>-1</sup>
MDO	a	 -232,880352	 _R-Ester -346,870541	 _R-Ester-H1 -346,221121	 -233,532302	-6,64
MDO	b	 -232,880352	 _R-Ester -346,870541	 _R-Ester-H2 -346,2291	 -233,532302	-27,59
MDO	c	 -232,880352	 AT_AC77_ 1 -384,911174	 AT_B_C7-H -384,259841	 -233,532302	-1,62
BMDO	a	 -232,880352	 AT_R0ouvMe -577,839086	 AT_R0ouvMe-H -577,206842	 -233,532302	-51,74
BMDO	c	 -232,880352	 At_A0mon -537,308006	 AT_B_0mon-H -536,677098	 -233,532302	-55,25

## ***Addition reactions***

**Ethyl°**

—•

AT\_\_ETHYL

Zero-point correction= 0.057280 (Hartree/Particle)

Thermal correction to Energy= 0.061299

Thermal correction to Enthalpy= 0.062243

Thermal correction to Gibbs Free Energy= 0.033086

Sum of electronic and zero-point Energies= -79.100587

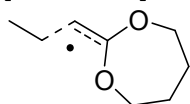
Sum of electronic and thermal Energies= -79.096569

Sum of electronic and thermal Enthalpies= -79.095625

Sum of electronic and thermal Free Energies= -79.124782

Tag	Symbol	X	Y	Z
1	C	-0.6940210	-0.0000020	-0.0007800
2	H	-1.1093840	-0.8876050	-0.4937660
3	H	-1.1093910	0.8875090	-0.4939310
4	H	-1.0958450	0.0000990	1.0288200
5	C	0.7952960	0.0000000	-0.0232180
6	H	1.3534830	0.9276920	0.0514320
7	H	1.3534860	-0.9276890	0.0514360

[Et<sup>o</sup>-MDO]\*

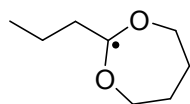


AT\_AC77-ET\_ts1

Zero-point correction= 0.209662 (Hartree/Particle)  
Thermal correction to Energy= 0.221437  
Thermal correction to Enthalpy= 0.222381  
Thermal correction to Gibbs Free Energy= 0.170332  
Sum of electronic and zero-point Energies= -464.008895  
Sum of electronic and thermal Energies= -463.997120  
Sum of electronic and thermal Enthalpies= -463.996176  
Sum of electronic and thermal Free Energies= -464.048225

Tag	Symbol	X	Y	Z
1	C	-4.3174480	-0.0061240	-0.3069380
2	H	-4.5608680	0.5704860	0.5949030
3	H	-4.4399240	-1.0694810	-0.0637940
4	C	-2.9342480	0.2928720	-0.8003570
5	C	-1.5124940	-0.3210110	0.9539250
6	H	-2.6460370	1.3380050	-0.8933330
7	H	-2.5159570	-0.3579640	-1.5646890
8	C	-0.2054950	-0.1996340	0.6008450
9	H	-1.9486020	0.4434160	1.5837190
10	H	-1.9595190	-1.3068050	0.9601570
11	O	0.5112190	0.9245980	0.8907220
12	O	0.3999680	-1.1470770	-0.1734540
13	C	1.2959870	1.5019800	-0.1730360
14	C	1.7747940	-1.4566090	0.1246360
15	C	2.7020510	0.9073760	-0.2194460
16	H	0.7744570	1.3793800	-1.1305270
17	H	1.3420130	2.5695370	0.0613860
18	C	2.7342980	-0.5618080	-0.6579490
19	H	1.9476670	-1.3855070	1.2060550
20	H	1.8994190	-2.5011100	-0.1761330
21	H	3.1435490	1.0116170	0.7805420
22	H	3.3154790	1.5109930	-0.9017770
23	H	2.4750870	-0.6423790	-1.7219770
24	H	3.7522330	-0.9593420	-0.5484120
25	H	-5.0931640	0.2367310	-1.0543410

Et – MDO°



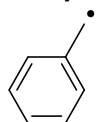
AT\_AC77-ET\_add1

Zero-point correction= 0.214797 (Hartree/Particle)  
 Thermal correction to Energy= 0.225837  
 Thermal correction to Enthalpy= 0.226781  
 Thermal correction to Gibbs Free Energy= 0.177121  
 Sum of electronic and zero-point Energies= -464.055786  
 Sum of electronic and thermal Energies= -464.044746  
 Sum of electronic and thermal Enthalpies= -464.043802  
 Sum of electronic and thermal Free Energies= -464.093461

Tag	Symbol	X	Y	Z
1	C	4.1261990	0.1232660	0.2337920
2	H	4.4446990	-0.9140010	0.3965180
3	H	4.1045550	0.6184400	1.2127230
4	C	2.7576040	0.1850660	-0.4503810
5	C	1.6532040	-0.4979670	0.3697670
6	H	2.8125890	-0.2892440	-1.4389170
7	H	2.4737920	1.2293780	-0.6272330
8	C	0.2967960	-0.4060590	-0.2709510
9	H	1.8879840	-1.5589410	0.5166770
10	H	1.6226470	-0.0466390	1.3805190
11	O	-0.6096170	-1.2863030	0.2678840
12	O	-0.1666880	0.8531480	-0.5807770
13	C	-1.8992780	-1.3513630	-0.3606810
14	C	-1.0964350	1.4773680	0.3329320
15	C	-2.8807580	-0.3636010	0.2698050
16	H	-1.7930230	-1.1805250	-1.4393980
17	H	-2.2441810	-2.3784060	-0.2050950
18	C	-2.5407430	1.1074490	-0.0012220
19	H	-0.8438800	1.2096470	1.3675960
20	H	-0.9409860	2.5532970	0.2077480
21	H	-2.8977090	-0.5509480	1.3517920
22	H	-3.8891390	-0.5849840	-0.1053710
23	H	-2.7084950	1.3432700	-1.0603830
24	H	-3.2135600	1.7536760	0.5788860
25	H	4.8956100	0.6162640	-0.3712750



### Benzyl°

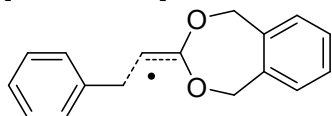


AT\_\_BZ1

Zero-point correction= 0.110386 (Hartree/Particle)  
Thermal correction to Energy= 0.116271  
Thermal correction to Enthalpy= 0.117216  
Thermal correction to Gibbs Free Energy= 0.081252  
Sum of electronic and zero-point Energies= -270.804757  
Sum of electronic and thermal Energies= -270.798872  
Sum of electronic and thermal Enthalpies= -270.797928  
Sum of electronic and thermal Free Energies= -270.833891

Tag	Symbol	X	Y	Z
1	C	0.0000000	0.0000000	-1.8397060
2	C	0.0000000	-1.2120300	-1.1338590
3	C	0.0000000	-1.2181660	0.2519670
4	C	0.0000000	0.0000000	0.9954720
5	C	0.0000000	1.2181660	0.2519670
6	C	0.0000000	1.2120300	-1.1338590
7	H	0.0000000	0.0000000	-2.9260170
8	H	0.0000000	-2.1538870	-1.6766190
9	H	0.0000000	-2.1611260	0.7933690
10	H	0.0000000	2.1611260	0.7933690
11	H	0.0000000	2.1538870	-1.6766190
12	C	0.0000000	0.0000000	2.4020830
13	H	0.0000000	-0.9284830	2.9640670
14	H	0.0000000	0.9284830	2.9640670

[Bz °– BMDO]\*

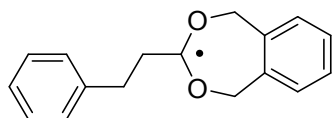


AT\_A0-BZts

Zero-point correction= 0.284255 (Hartree/Particle)  
 Thermal correction to Energy= 0.300969  
 Thermal correction to Enthalpy= 0.301913  
 Thermal correction to Gibbs Free Energy= 0.236373  
 Sum of electronic and zero-point Energies= -808.107881  
 Sum of electronic and thermal Energies= -808.091167  
 Sum of electronic and thermal Enthalpies= -808.090223  
 Sum of electronic and thermal Free Energies= -808.155763

Tag	Symbol	X	Y	Z
1	C	1.8702840	-1.3882750	0.0053040
2	C	0.2675680	0.1980640	0.7370300
3	C	2.1848570	1.5681920	0.5648620
4	H	1.3356440	-1.3227860	-0.9513890
5	H	2.0197810	-2.4464780	0.2355400
6	H	2.3346930	2.5928370	0.2137260
7	O	1.0124360	-0.8971990	1.0558790
8	C	3.3429370	0.6983120	0.1213680
9	C	3.2089540	-0.6860940	-0.0812080
10	C	4.3378800	-1.4366910	-0.4284150
11	C	5.5869300	-0.8366230	-0.5828880
12	C	5.7190770	0.5371300	-0.3840650
13	C	4.5999170	1.2926450	-0.0368630
14	H	6.6852550	1.0198700	-0.5018760
15	H	6.4497160	-1.4393390	-0.8525610
16	H	4.2349010	-2.5093650	-0.5786430
17	H	4.7016210	2.3654730	0.1137030
18	O	0.9080790	1.1730460	0.0304900
19	H	2.1173670	1.5951820	1.6610940
20	C	-1.0857590	0.2457120	0.9434060
21	H	-1.5619790	1.2183760	0.9600400
22	H	-1.5271590	-0.5300650	1.5567990
23	C	-2.1900710	-0.3758900	-0.8645010
24	C	-3.5866260	-0.2072510	-0.5601750
25	H	-1.7192070	0.3349600	-1.5370810
26	C	-4.3424320	-1.2477910	0.0346910
27	C	-4.2458790	1.0258760	-0.7904170
28	C	-5.6790170	-1.0665080	0.3706820
29	H	-3.8618790	-2.2056400	0.2229730
30	C	-5.5827360	1.2023490	-0.4525560
31	H	-3.6900060	1.8422410	-1.2468510

32 C	-6.3109570	0.1591280	0.1307980
33 H	-6.2362480	-1.8850200	0.8201570
34 H	-6.0647230	2.1575500	-0.6469600
35 H	-7.3560840	0.2986010	0.3929630
36 H	-1.7953740	-1.3868710	-0.9149040

**Bz – BMDO°**

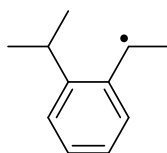
## AT\_A0-BZadd

Zero-point correction= 0.288053 (Hartree/Particle)  
 Thermal correction to Energy= 0.304546  
 Thermal correction to Enthalpy= 0.305491  
 Thermal correction to Gibbs Free Energy= 0.240411  
 Sum of electronic and zero-point Energies= -808.140345  
 Sum of electronic and thermal Energies= -808.123852  
 Sum of electronic and thermal Enthalpies= -808.122908  
 Sum of electronic and thermal Free Energies= -808.187988

Tag	Symbol	X	Y	Z
1	C	-2.3596450	-1.7490250	0.0197610
2	C	-0.2397770	-0.7635040	0.3511390
3	C	-1.6192230	1.1787540	0.2403130
4	H	-2.2371830	-2.0425710	1.0711630
5	H	-2.6937580	-2.6278210	-0.5391320
6	H	-1.6039250	2.1350400	0.7709450
7	O	-1.0717240	-1.4208440	-0.5199760
8	C	-3.0491370	0.7163730	0.0520170
9	C	-3.3844070	-0.6401420	-0.1081640
10	C	-4.7198760	-0.9889840	-0.3401620
11	C	-5.7213150	-0.0211520	-0.4063570
12	C	-5.3895680	1.3232580	-0.2431240
13	C	-4.0614100	1.6805250	-0.0138640
14	H	-6.1582940	2.0897160	-0.2901750
15	H	-6.7512530	-0.3160430	-0.5876270
16	H	-4.9772960	-2.0380130	-0.4716700
17	H	-3.8024970	2.7291420	0.1181600
18	O	-0.8157040	0.2808710	1.0385470
19	H	-1.1320290	1.3273520	-0.7333860
20	C	1.1512760	-0.5682410	-0.1797140
21	H	1.1626480	0.2353880	-0.9388240
22	H	1.4553390	-1.4838550	-0.6981780
23	C	2.1655770	-0.2205880	0.9313720
24	C	3.5601020	0.0154870	0.3922710
25	H	1.8099140	0.6695110	1.4622920
26	C	4.4565470	-1.0493280	0.2275710
27	C	3.9786650	1.2984250	0.0140990
28	C	5.7309850	-0.8413880	-0.3012810
29	H	4.1528020	-2.0518570	0.5225350
30	C	5.2518230	1.5125910	-0.5160360
31	H	3.3000420	2.1394440	0.1422890
32	C	6.1329940	0.4419110	-0.6763070

33 H	6.4116820	-1.6811860	-0.4162450
34 H	5.5571790	2.5168740	-0.7989800
35 H	7.1262550	0.6067790	-1.0854640
36 H	2.1781280	-1.0379400	1.6625230

iP-STY°

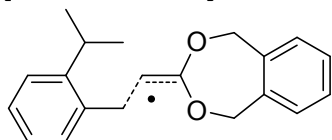


AT\_\_iP-STY

Zero-point correction= 0.219558 (Hartree/Particle)  
 Thermal correction to Energy= 0.231487  
 Thermal correction to Enthalpy= 0.232431  
 Thermal correction to Gibbs Free Energy= 0.181590  
 Sum of electronic and zero-point Energies= -427.953629  
 Sum of electronic and thermal Energies= -427.941700  
 Sum of electronic and thermal Enthalpies= -427.940756  
 Sum of electronic and thermal Free Energies= -427.991597

Tag	Symbol	X	Y	Z
1	C	-1.1656180	-1.6213210	-0.2013340
2	C	-0.8628220	-0.2415100	-0.0908070
3	C	0.4914970	0.2588840	-0.1027420
4	C	-1.9201730	0.7079540	0.0382090
5	C	0.6958990	1.6310300	0.0220900
6	C	-1.6778080	2.0665340	0.1589500
7	H	-2.9452580	0.3508620	0.0417040
8	C	-0.3622350	2.5388020	0.1537810
9	H	1.7096140	2.0189180	0.0143530
10	H	-2.5098080	2.7593370	0.2564090
11	H	-0.1561990	3.6015500	0.2470520
12	H	-0.3519930	-2.3303930	-0.2993480
13	C	-2.5534870	-2.1888160	-0.1995500
14	H	-3.1633560	-1.8010600	-1.0294780
15	H	-2.5295710	-3.2784680	-0.2925440
16	H	-3.1008460	-1.9493030	0.7243920
17	C	1.6776150	-0.6965500	-0.2090220
18	H	1.3910640	-1.5058670	-0.8928100
19	C	1.9943000	-1.3337810	1.1619640
20	H	2.3124570	-0.5649530	1.8761950
21	H	1.1187910	-1.8376300	1.5838810
22	H	2.8033020	-2.0692170	1.0722130
23	C	2.9467540	-0.0642400	-0.8040460
24	H	2.7411220	0.4351600	-1.7571630
25	H	3.3980220	0.6698850	-0.1264930
26	H	3.6991360	-0.8407390	-0.9833210

[iP-STY ° – BMDO]\*



AT\_A0-iP-STYts2

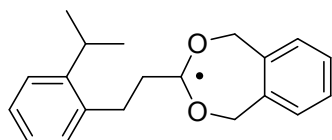
Zero-point correction= 0.393563 (Hartree/Particle)  
 Thermal correction to Energy= 0.416146  
 Thermal correction to Enthalpy= 0.417090  
 Thermal correction to Gibbs Free Energy= 0.339230  
 Sum of electronic and zero-point Energies= -965.253046  
 Sum of electronic and thermal Energies= -965.230463  
 Sum of electronic and thermal Enthalpies= -965.229519  
 Sum of electronic and thermal Free Energies= -965.307378

Tag	Symbol	X	Y	Z
1	C	-2.6461020	-1.5264110	0.3205030
2	C	-0.8479280	-0.5707690	-0.9011920
3	C	-2.4701910	1.1361350	-1.1117630
4	H	-2.0467420	-1.2697240	1.2040410
5	H	-2.9942730	-2.5560180	0.4381240
6	H	-2.4098420	2.2273050	-1.0724240
7	O	-1.7873670	-1.5560670	-0.8368560
8	C	-3.7344420	0.6659020	-0.4221570
9	C	-3.8329180	-0.5948180	0.1915290
10	C	-5.0538420	-0.9859280	0.7529450
11	C	-6.1677460	-0.1480960	0.7203550
12	C	-6.0689250	1.1032920	0.1133110
13	C	-4.8569580	1.5010900	-0.4494750
14	H	-6.9273360	1.7684940	0.0804360
15	H	-7.1055540	-0.4731540	1.1621800
16	H	-5.1312880	-1.9646210	1.2219020
17	H	-4.7782690	2.4796640	-0.9187790
18	O	-1.2530750	0.6705110	-0.5002290
19	H	-2.4709300	0.8374830	-2.1691290
20	C	0.4773070	-0.8272130	-1.1632260
21	H	1.0745100	-0.0036850	-1.5356340
22	H	0.7239790	-1.8134340	-1.5400840
23	C	1.6568490	-1.0565340	0.6543890
24	C	3.0158150	-0.7461580	0.2328870
25	C	3.4852020	0.6028740	0.1233750
26	C	3.9020130	-1.7874230	-0.1322320
27	C	4.7922650	0.8242330	-0.3175710
28	C	2.6024390	1.7835010	0.5298660
29	C	5.1968190	-1.5367020	-0.5711650
30	H	3.5653530	-2.8168700	-0.0599730
31	C	5.6515550	-0.2218150	-0.6645000

32	H	5.1597040	1.8430450	-0.3963510
33	H	1.5606250	1.5204630	0.3146000
34	C	2.8854800	3.0784180	-0.2517030
35	C	2.7101720	2.0464090	2.0478720
36	H	5.8484130	-2.3657070	-0.8363680
37	H	6.6611440	-0.0066670	-1.0043820
38	H	3.8607650	3.5101190	0.0012880
39	H	2.8618620	2.9097080	-1.3341100
40	H	2.1276130	3.8322430	-0.0087200
41	H	2.4668580	1.1511870	2.6300200
42	H	3.7308330	2.3471320	2.3137660
43	H	2.0284820	2.8493260	2.3551330
44	H	1.1450470	-0.2702180	1.1989100
45	C	1.2789050	-2.4426670	1.1168880
46	H	0.2090280	-2.4924880	1.3446050
47	H	1.4841250	-3.2139130	0.3651510
48	H	1.8248200	-2.7291580	2.0288590



iP-STY – BMDO°



AT\_A0-iP-STYadd2

Zero-point correction= 0.397096 (Hartree/Particle)  
 Thermal correction to Energy= 0.419405  
 Thermal correction to Enthalpy= 0.420350  
 Thermal correction to Gibbs Free Energy= 0.342712  
 Sum of electronic and zero-point Energies= -965.282138  
 Sum of electronic and thermal Energies= -965.259829  
 Sum of electronic and thermal Enthalpies= -965.258885  
 Sum of electronic and thermal Free Energies= -965.336522

Tag	Symbol	X	Y	Z
1	C	-3.1319430	-1.8460960	-0.0772400
2	C	-0.8966780	-1.1447540	0.2174600
3	C	-2.0171250	0.9615480	0.1391580
4	H	-3.0288410	-2.1591530	0.9706350
5	H	-3.5863430	-2.6712250	-0.6330280
6	H	-1.8690990	1.9046820	0.6727150
7	O	-1.8221610	-1.6833030	-0.6396970
8	C	-3.4977840	0.6871830	-0.0222300
9	C	-4.0072840	-0.6139250	-0.1817420
10	C	-5.3804930	-0.7866480	-0.3903380
11	C	-6.2501090	0.3022700	-0.4340000
12	C	-5.7455090	1.5918890	-0.2713480
13	C	-4.3786020	1.7739110	-0.0651920
14	H	-6.4100540	2.4510030	-0.3010240
15	H	-7.3124500	0.1432020	-0.5974480
16	H	-5.7731970	-1.7929180	-0.5215950
17	H	-3.9844860	2.7796310	0.0662510
18	O	-1.3185970	-0.0359900	0.9182800
19	H	-1.5338160	1.0524460	-0.8434660
20	C	0.4996090	-1.1237100	-0.3356920
21	H	0.5942880	-0.3082930	-1.0758560
22	H	0.6717030	-2.0560790	-0.8854180
23	C	1.5886900	-0.9442520	0.7544930
24	C	2.9468430	-0.6806570	0.1013920
25	C	3.4151350	0.6311770	-0.1588460
26	C	3.7418980	-1.7671750	-0.2925410
27	C	4.6688840	0.7869700	-0.7686500
28	C	2.6191900	1.8745470	0.2456590
29	C	4.9799900	-1.5935350	-0.9080840
30	H	3.3877540	-2.7775680	-0.1107140
31	C	5.4508230	-0.3042240	-1.1424430

32	H	5.0454620	1.7874550	-0.9602470
33	H	1.5590420	1.6028710	0.2870350
34	C	2.7226440	3.0324160	-0.7637210
35	C	3.0289580	2.3487150	1.6553020
36	H	5.5696200	-2.4596690	-1.1973510
37	H	6.4165290	-0.1445750	-1.6152200
38	H	3.7242160	3.4766080	-0.7851020
39	H	2.4796400	2.7020660	-1.7797070
40	H	2.0236340	3.8308640	-0.4883030
41	H	2.8932490	1.5566800	2.3998350
42	H	4.0859190	2.6407480	1.6712110
43	H	2.4323220	3.2151780	1.9662770
44	H	1.3068120	-0.0653030	1.3408870
45	C	1.5907230	-2.1294940	1.7358530
46	H	0.6265450	-2.1838320	2.2514450
47	H	1.7404120	-3.0894930	1.2288030
48	H	2.3800350	-2.0179210	2.4872070

PCN°

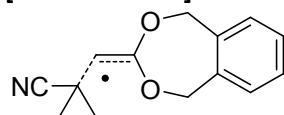


AT\_\_AZO

Zero-point correction= 0.085196 (Hartree/Particle)  
Thermal correction to Energy= 0.091784  
Thermal correction to Enthalpy= 0.092728  
Thermal correction to Gibbs Free Energy= 0.054456  
Sum of electronic and zero-point Energies= -210.652127  
Sum of electronic and thermal Energies= -210.645539  
Sum of electronic and thermal Enthalpies= -210.644595  
Sum of electronic and thermal Free Energies= -210.682866

Tag	Symbol	X	Y	Z
1	C	0.3090130	0.0000000	0.0000230
2	C	1.0652260	1.2972370	-0.0000040
3	H	0.3985080	2.1626210	-0.0000080
4	H	1.7195780	1.3641690	0.8813690
5	H	1.7195410	1.3641570	-0.8814100
6	C	-1.0827300	-0.0000040	0.0000190
7	C	1.0652380	-1.2972300	-0.0000030
8	H	0.3985250	-2.1626210	0.0002560
9	H	1.7193490	-1.3642660	-0.8815500
10	H	1.7197820	-1.3640460	0.8812340
11	N	-2.2593950	-0.0000040	-0.0000140

[PCN °– BMDO]\*

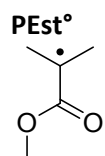


AT\_A0-AZOts7

Zero-point correction= 0.259488 (Hartree/Particle)  
 Thermal correction to Energy= 0.276360  
 Thermal correction to Enthalpy= 0.277304  
 Thermal correction to Gibbs Free Energy= 0.212990  
 Sum of electronic and zero-point Energies= -747.954541  
 Sum of electronic and thermal Energies= -747.937669  
 Sum of electronic and thermal Enthalpies= -747.936725  
 Sum of electronic and thermal Free Energies= -748.001039

Tag	Symbol	X	Y	Z
1	C	0.9068210	1.3364520	-0.2583910
2	C	-0.6829860	-0.3785380	-0.6968260
3	C	1.2392760	-1.6757300	-0.2351020
4	H	0.4015600	1.4295340	0.7117930
5	H	1.0356040	2.3409980	-0.6685470
6	H	1.3927750	-2.5918610	0.3412300
7	O	0.0198550	0.6765400	-1.1850400
8	C	2.3984440	-0.7265110	-0.0179340
9	C	2.2552250	0.6691450	-0.0949930
10	C	3.3874670	1.4795990	0.0472630
11	C	4.6484520	0.9285560	0.2702260
12	C	4.7892380	-0.4563880	0.3501630
13	C	3.6673410	-1.2716570	0.2079080
14	H	5.7647720	-0.9012330	0.5252360
15	H	5.5136120	1.5768080	0.3767760
16	H	3.2772030	2.5598810	-0.0184040
17	H	3.7767310	-2.3521970	0.2737150
18	O	-0.0394500	-1.1709110	0.2042940
19	H	1.1582300	-1.9544490	-1.2945680
20	C	-3.3713400	0.2479190	0.5023230
21	C	-2.0082100	-0.5736630	-1.0084320
22	H	-2.4192200	0.0288570	-1.8099040
23	H	-2.4003860	-1.5780550	-0.9012460
24	C	-3.0338380	1.7240000	0.5326800
25	H	-3.2011660	2.2018260	-0.4374370
26	H	-3.6473340	2.2538230	1.2764730
27	H	-1.9841450	1.8671430	0.8125880
28	C	-4.6029890	-0.0867180	-0.1278930
29	C	-3.0327830	-0.5430670	1.7495490
30	H	-3.2627220	-1.6060580	1.6296340
31	H	-1.9670280	-0.4480700	1.9822290
32	H	-3.6021170	-0.1740400	2.6157820

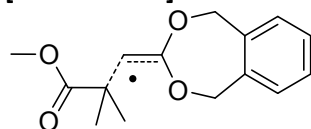
33 N            -5.5771880 -0.3911900 -0.6989460



**AT\_MMA2**

Zero-point correction= 0.128067 (Hartree/Particle)  
 Thermal correction to Energy= 0.137378  
 Thermal correction to Enthalpy= 0.138322  
 Thermal correction to Gibbs Free Energy= 0.092461  
 Sum of electronic and zero-point Energies= -346.241559  
 Sum of electronic and thermal Energies= -346.232249  
 Sum of electronic and thermal Enthalpies= -346.231305  
 Sum of electronic and thermal Free Energies= -346.277165

Tag	Symbol	X	Y	Z
1	C	-1.4493950	1.5702980	-0.0009640
2	H	-2.0112480	1.8291970	0.9100160
3	H	-0.5719710	2.2148610	-0.0587350
4	H	-2.1165130	1.8058380	-0.8436260
5	C	-1.0904180	0.1195560	-0.0035640
6	C	0.2875500	-0.3505210	-0.0012890
7	C	2.5687160	0.2440480	0.0011700
8	H	3.1581350	1.1621360	0.0044630
9	H	2.7929300	-0.3517290	-0.8885420
10	H	2.7902880	-0.3565500	0.8882520
11	O	0.6218770	-1.5302930	-0.0009550
12	O	1.2002540	0.6644350	0.0002920
13	C	-2.1805860	-0.9008310	0.0019450
14	H	-2.8319550	-0.7746380	0.8800530
15	H	-1.7713280	-1.9123630	0.0082080
16	H	-2.8305930	-0.7851910	-0.8785720

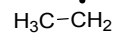
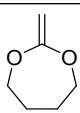
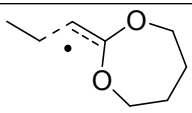
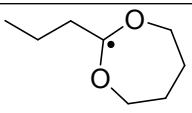
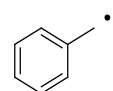
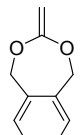
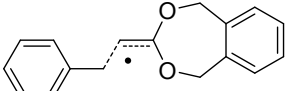
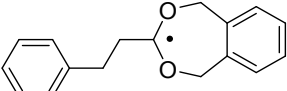
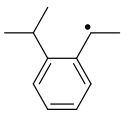
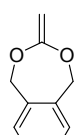
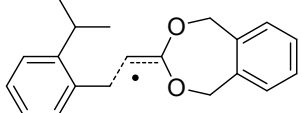
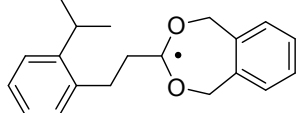
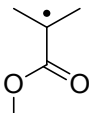
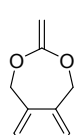
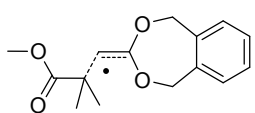

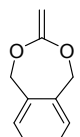
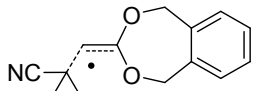
**[PEst°-BMDO]\***

## AT\_A0-MMAts

Zero-point correction= 0.302265 (Hartree/Particle)  
 Thermal correction to Energy= 0.321900  
 Thermal correction to Enthalpy= 0.322844  
 Thermal correction to Gibbs Free Energy= 0.251949  
 Sum of electronic and zero-point Energies= -883.545380  
 Sum of electronic and thermal Energies= -883.525745  
 Sum of electronic and thermal Enthalpies= -883.524801  
 Sum of electronic and thermal Free Energies= -883.595696

Tag	Symbol	X	Y	Z
1	C	0.0000000	0.0000000	0.0000000
2	C	0.0000000	0.0000000	2.3784905
3	C	2.3242057	0.0000000	1.9465326
4	H	-0.2532542	1.0639176	0.0925099
5	H	-0.6748230	-0.4439517	-0.7359960
6	H	3.1610985	0.5450276	2.3913833
7	O	-0.3209567	-0.6663562	1.2377678
8	C	2.5154428	-0.1075786	0.4481442
9	C	1.4354869	-0.1703688	-0.4486733
10	C	1.6928141	-0.3369932	-1.8144576
11	C	2.9962567	-0.4349680	-2.2991041
12	C	4.0674459	-0.3700282	-1.4087589
13	C	3.8209239	-0.2052593	-0.0465948
14	H	5.0891698	-0.4432109	-1.7707402
15	H	3.1720531	-0.5649752	-3.3632558
16	H	0.8561775	-0.3917139	-2.5077055
17	H	4.6568379	-0.1499146	0.6477620
18	O	1.1483593	0.7307414	2.3502944
19	H	2.2903815	-0.9973302	2.4063028
20	C	-0.8514431	0.0346471	3.4632289
21	H	-0.4099706	0.2454642	4.4310675
22	H	-1.6824170	-0.6619600	3.4439499
23	C	-2.1046443	1.7986723	3.5081611
24	C	-1.1158724	2.9301716	3.6425612
25	C	-2.8002984	1.4370644	4.7529242
26	C	-2.8715648	1.7352684	2.2093709
27	H	-0.6052115	2.8938456	4.6074340
28	H	-0.3695550	2.8981440	2.8418563
29	H	-1.6299394	3.9019036	3.5778068
30	O	-2.4154077	1.7053507	5.8826862
31	O	-3.9155707	0.6756320	4.5320433

32	H	-3.5897401	2.5666146	2.1385649
33	H	-2.1897160	1.8284164	1.3559735
34	H	-3.4362213	0.8058888	2.1060087
35	C	-4.5932626	0.2399553	5.7151461
36	H	-4.9367449	1.0952164	6.3044633
37	H	-5.4439241	-0.3489392	5.3677367
38	H	-3.9353565	-0.3708087	6.3405509

Sum of electronic and thermal Enthalpies (Hartree)				$\Delta H^\ddagger$	$\Delta H_r$
Radical	Monomer	Transition state	product	(kJ.mol <sup>-1</sup> )	(kJ.mol <sup>-1</sup> )
 H <sub>3</sub> C-CH <sub>2</sub> -79,095625	 -384,911174	 -463,996176	 -464.043802	27.89	-97.15
 -270,797928	 -537,308006	 -808,090223	 -808,122908	41.25	-42.58
 -427,940756	 -537,308006	 -965,229519	 -965,258885	50.52	-22.37
 -346,231305	 -537,308006	 -883,524801	-	38.1	-
 -210,644595	 -537,308006	 -747,936725	-	41.68	-



## References

1. <http://www.wako-chem.co.jp/specialty/oilazo/VAm-111.htm>
2. F. Chauvin, P. E. Dufils, D. Gimes, Y. Guillaneuf, S. R. A. Marque, P. Tordo and D. Bertin, *Macromolecules*, 2006, **39**, 5238-5250.
3. A. Tardy, V. Delplace, D. Siri, C. Lefay, S. Harrisson, B. de Fatima Albergaria Pereira, L. Charles, D. Gimes, J. Nicolas and Y. Guillaneuf, *Polymer Chemistry*, 2013, **4**, 4776-4787.