Degradable Polystyrene via the Cleavable Comonomer Approach

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1. Materials

All reagents and solvents were used as received. Diphenic anhydride (98%), sodium borohydride (NaBH₄) (99%), Lawesson reagent (97%), styrene (99%), ethanolamine (99.5%), anisole (99%) and anhydrous tolune (99.8%) were purchased from Sigma-Aldrich. 3,6,9-Triethyl-3,6,9-trimethyl-1,4,7-triperoxonane (Trigonox® 301) was purchased from Acros Organics. Ammonia solution (25%) was purchased from Fisher Chemicals. Dimethylformamide (DMF-for analysis) was purchased from Carlo Erba Reagents. Potassium hydroxide and sodium hydroxide were purchased from Merck. Phenylglyoxylic acid was purchased from TCI. Deuterated chloroform (CDCl₃) was obtained from Sigma-Aldrich. Dibenzo[c,e]-oxepane-5-thione (DOT) was synthetized according to the literature procedure.¹

2. Analytical methods

a. Nuclear Magnetic Resonance Spectroscopy (NMR)

¹H and ¹³C spectra were obtained on a Bruker Avance DPX 300 MHz spectrometer at 300 MHz (¹H), 75.5 MHz (¹³C). Tetramethylsilane (TMS) was used as internal standard. The ¹H chemical shifts were referenced to the solvent peak for CDCl₃ (δ = 7.26 ppm) and the ¹³C chemical shifts were referenced to the solvent peak for CDCl₃ (δ = 77.16 ppm).

b. Size Exclusion Chromatography (SEC)

Molar masses were determined by size exclusion chromatography (SEC). The apparatus was equipped with a 1260 infinity pump (Agilent Technologies), a 1260 infinity autosampler (Agilent Technologies), a 1260 infinity UV photodiode array detector (Agilent Technologies), a 1260 infinity RI detector (Agilent Technologies). The stationary phase was composed of 2 PSS-SDV Linear M column and a precolumn at 40 °C. Mobile phase was THF at 1 mL.min⁻¹. Samples were solubilized in a mixture of THF and toluene (0.25wt%) and filtered through 0.45 µm PTFE syringe filter (Agilent). Samples concentration was about 2.5 mg.mL⁻¹. The system was calibrated using polystyrene (PS) standards in the range 100 - 400 000 g.mol⁻¹, purchased from Agilent.

c. Thermogravimetric Analysis (TGA)

TGA measurements were performed on a PerkinElmer 8000 instrument at a scan rate of 10 °C.min⁻¹ from 30 °C to 800 °C under nitrogen atmosphere.

d. Differential Scanning Analysis (DSC)
Differential scanning calorimetry (DSC) analyses were performed on a TA Instruments (DSC Q20) with the following program (heat-cool-heat cycle): heat from 25 °C to 200 °C at 10 °C.min⁻¹, cool to -50 °C at 5 °C.min⁻¹ and heat to 200 °C at 10 °C.min⁻¹. Heat curves from the second heating are used here.

3. Copolymerization

a. Synthesis of P1-P3

In a 10mL vial, fitted with a rubber septum and a magnetic stirrer bar, styrene, MDO and DTBP were degassed with argon. The mixture was then immersed 6h in a preheated oil bath at 120 °C. The copolymer was then precipitated twice in cold methanol and dried under high vacuum.

| Ratio S/MDO | n_{styrene} (mol) | n_{MDO} (mol) | n_{DTBP} (mol) |
|-------------|-------------------|---------------|----------------|
| P1 80/20    | 7.01 10⁻³         | 1.75 10⁻³     | 8.77 10⁻⁵      |
| P2 50/50    | 1.75 10⁻³         | 1.75 10⁻³     | 3.51 10⁻⁵      |
| P3 50/50    | 8.77 10⁻³         | 8.77 10⁻³     | 1.75 10⁻⁵      |

b. Synthesis of P4-P7

In a 10mL vial, fitted with a rubber septum and a magnetic stirrer bar, styrene, DOT, AIBN and anisole were degassed with argon. The mixture was then immersed in a preheated oil bath at 80 °C. The copolymer was then precipitated twice in cold methanol and dried under high vacuum.

| Ratio S/DOT | n_{styrene} (mol) | n_{DOT} (mol) | n_{AIBN} (mol) | n_{anisole} (mol) | Time (h) |
|-------------|-------------------|---------------|----------------|-------------------|----------|
| P4 95/5     | 4.2 10⁻³          | 2.21 10⁻⁴    | 4.2 10⁻⁵       | 1.84 10⁻²        | 24       |
| P5 70/30    | 1.03 10⁻³         | 4.42 10⁻⁴    | 1.47 10⁻⁵      | 6.44 10⁻³        | 24       |
| P6 50/50    | 4.42 10⁻⁴         | 4.42 10⁻⁴    | 8.85 10⁻⁶      | 3.68 10⁻³        | 24       |
| P7 95/5     | 4.2 10⁻³          | 2.21 10⁻⁴    | 4.2 10⁻⁵       | 4.6 10⁻⁴         | 5        |
Figure S1: Kinetic plot of the anisole (10 mol%) copolymerization styrene (red squares) and DOT (blue squares) with feed ratio \([\text{Styrene}]_0 : [\text{DOT}]_0 = 95 : 5\).

c. Synthesis of PS1–PS3

In a 10mL vial, fitted with a rubber septum and a magnetic stirrer bar, styrene and anisole were degassed with argon. The mixture was then immersed in a preheated oil bath at 150°C. The copolymer was then precipitated twice in cold methanol and dried under high vacuum.

| n_{styrene} (mol) | n_{TG301} (mol) | Anisole (in mL) | Time (h) | PS conversion (%) |
|-------------------|------------------|-----------------|----------|-------------------|
| PS1               | 0.04801          | 0               | 20       | 17                | 100               |
| PS2               | 0.05761          | 0.00058         | 9        | 2                 | 100               |
| PS3               | 0.04801          | 0               | 0.2      | 1.75              | 100               |

d. Synthesis of Copo1 – Copo3

In a 10mL vial, fitted with a rubber septum and a magnetic stirrer bar, a mixture of DOT, styrene, and anisole was degassed with argon. The mixture was then immersed in a preheated oil bath at 150°C. The copolymer was then precipitated twice in cold methanol and dried under high vacuum.

| n_{styrene} (mol) | n_{DOT} (mol) | n_{TG301} (mol) | Anisole (in mL) | Time (min) | PS conversion (%) | pDOT conversion (%) |
|-------------------|---------------|-----------------|-----------------|------------|-------------------|---------------------|
| Copo1             | 0.0017695     | 0.0004424       | 0               | 1          | 20                | 41                  | 48                  |
| Copo2             | 0.00420261    | 0.00022119      | 4.4238E-05      | 1.5        | 2                 | 91                  | 93                  |
| Copo3             | 0.0084052     | 0.0004424       | 0               | 0.1        | 17                | 94                  | 96                  |
Figure S2: $^{13}$C and $^1$H NMR of Copo3
Figure S3: Loss of color of Copo2, t = 0 (left) and precipitated polymer (right).

4. PREDICI Simulations

To perform the PREDICI simulations, we used the scheme described below, that use many kinetic rate constants that are quite well described. The dissociation of AIBN is well known ($A = 2.910^{15}$ s$^{-1}$ and $E_a = 130.2$ kJ.mol$^{-1}$) and is set to $k_d = 1.5 \times 10^{-3}$ s$^{-1}$ at 80°C; An average efficiency of 60% was used to take the cage effect into account for the whole polymerization process.

$$
\begin{align*}
I - I & \xrightarrow{k_d f} 2 \ I' \\
I' + \text{styrene} & \rightarrow \text{Ps} (1) \\
\text{Ps} (n) + \text{styrene} & \xrightarrow{k_{p,S}} \text{Ps} (n+1) \\
\text{Ps} (m) + \text{Ps} (n) & \xrightarrow{k_t} \text{dead chains}
\end{align*}
$$

Scheme S1. PREDICI simulation of styrene polymerization in 10-80 mol% anisole.

The propagation rate constant of styrene has been widely studied and led to a IUPAC-related publication ($k_{p,S} = 4.27 \times 10^7$ s$^{-1}$ and $E_a = 32.5$ kJ.mol$^{-1}$). The termination reaction of polystyrene is mainly due by combination and its rate constant is usually between $10^7$ and $10^9$ L.mol$^{-1}$.s$^{-1}$. We thus chose an average value of $1.5 \times 10^8$ L.mol$^{-1}$.s$^{-1}$. To ensure that our simulations gave truthful data, we performed three polymerizations of styrene using various amount of solvent (10 or 80 mol% of anisole) and temperature (80 and 150 °C). The results are presented on Figure S4. The polymerization at 150 °C was performed using the Trigonox 301 as thermal initiator. Its complex mechanism impeded to implement its $k_d$ value into the scheme and we kept the same radical flux for the simulation ($k_d = 1.5 \times 10^{-3}$ s$^{-1}$). The dependance of $k_t$ value versus viscosity was not taken into account and this led to differences in the rate of polymerization when a high amount of solvent is used. Nevertheless, the scheme and rate constants are
consistent with the experimental data and could be used to model the copolymerization with the DOT monomer.

**Figure S4.** Kinetic plot of the anisole homopolymerization of styrene using 1 mol% of AIBN (10 mol% at 80 °C blue squares), (80 mol% at 80 °C red dots). The homopolymerization at 150 °C was performed using 1 mol% of Trigonox 301 with 80 mol% of anisole (turquoise diamonds). The solid lines are the PREDICI simulations using the kinetic rate constant given in the text.

The copolymerization of styrene with DOT were then simulated using the same scheme and rate constants but with adding 3 more propagation rate constants:

\[
P_{\text{DOT}}(n) + \text{Bu} \xrightarrow{k_{p,\text{DOT}}} P_{\text{DOT}}(n+1)
\]

\[
P_\text{S}(n) + \text{Bu} \xrightarrow{k_{p,\text{S}} / r_\text{S}} P_{\text{DOT}}(n+1)
\]

\[
P_{\text{DOT}}(n) + \text{Bu} \xrightarrow{k_{p,\text{DOT}} / r_{\text{DOT}}} P_\text{S}(n+1)
\]

**Scheme S2.** PREDICI simulation of the styrene-DOT copolymerization in 10-80 mol% anisole.
To simplify the scheme, we neglected the initiation of $P_{\text{DOT}}$ by the thermal initiator and we used the same rate constant for the various termination between $P_S$ and $P_{\text{DOT}}$ macroradicals.

The $r_S$, $r_{\text{DOT}}$ and $k_{p,\text{DOT}}$ was obtained by fitting the simulated and experimental data obtained at 80 °C. This led to $r_S = 2.0$, a $r_{\text{DOT}} = 0.36$ and a $k_{p,\text{DOT}} = 30 \text{ L.mol}^{-1}.\text{s}^{-1}$. To investigate the temperature effect and thus the increase of temperature to 150 °C, we chose to keep the activation energy that is obtained by DFT calculations for the $r_S$, $r_{\text{DOT}}$ and $k_{p,\text{DOT}}$.

\[
E_{a,p,S} = 40.1 \text{ kJ.mol}^{-1}
\]

\[
E_{a,\text{addDOT/S}} = 25.0 \text{ kJ.mol}^{-1}
\]

\[
r_S = \frac{k_{p,S}}{k_{trS/DOT}} \quad r_{\text{DOT}} = \frac{k_{tr\text{DOT/DOT}}}{k_{\text{addDOT/S}}} \quad k_{p,\text{DOT}} = k_{tr\text{DOT/DOT}}
\]

Activation energy for $r_S$: $E_{a,p,S} - (E_{a,\text{add}} + E_{a,p} - E_{a,\text{add}}) = 40.1 - (29 + 62.6 - 41.2) = -10.3 \text{ kJ.mol}^{-1}$

Activation energy for $r_{\text{DOT}}$: $E_{a,\text{add}} + E_{a,p} - E_{a,\text{add}} - E_{a,\text{addDOT/S}} = 27.3 + 61.5 - 47.3 - 25.0 = 16.5 \text{ kJ.mol}^{-1}$

Activation energy for $k_{p,\text{DOT}}$: $E_{a,\text{add}} + E_{a,p} - E_{a,\text{add}} = 27.3 + 61.5 - 47.3 = 41.5 \text{ kJ.mol}^{-1}$
5. Mechanical & Rheological properties

a. Samples preparation and apparatus
All polymers (powders) were melt-pressed in heated pellet dies at 150°C to obtain defect-free, ca. 1 mm-thick films. Pressed samples were either directly used for rheology (8 mm-diameter disks) or cut into rectangular shapes (ca 20 x 5 mm²) for DMA analysis.

b. Dynamic mechanical analysis
DMA analysis was performed on a DMA 1 apparatus (Mettler Toledo) in the tension film mode. Rectangular samples (see above) were tested at 1 Hz and an amplitude of 10 μm while applying a heating ramp from 25 to 150°C at 3 K.min⁻¹.

c. Rheology
Melt-pressed samples were analyzed with a MARS 60 rheometer (Thermo Scientific) equipped with 8 mm parallel-plate geometries and a Peltier module. After initial setup of samples at 150°C, a series of stress-controlled oscillations (500 Pa, 50 to 0.01 Hz) were run every 10°C from 120 to 190°C. Master curves were obtained by conventional time-temperature superposition using a reference temperature of 120°C.

6. Copolymer degradation

a. Procedures

Degradation of P1-P3:
In a 5 mL vial, 15 mg of copolymer was dissolved in 0.750 mL of THF. After solubilization, 0.750 mL of KOH 5 wt% in MeOH was added. The cloudy mixture was stirred at room temperature during 96 h. Sample was dried under vacuum, then 1.5mL of chloroform were added. Salts were removed by filtration, solvent was removed under pressure and degradation products were analyzed by SEC.

Degradation of P4-P7:
In a 5 mL vial, 15 mg of copolymer was dissolved in 0.750 mL of THF. After solubilization, 0.750 mL of degradation solution (KOH 5 wt% in MeOH or TBD 2.5 wt% in THF or iPrNH₂ 50 wt% in DCM) was added. The cloudy mixture was stirred at room temperature during 17. Sample was dried under vacuum:
- For the degradation with KOH, 1.5mL of chloroform were added. Salts were removed by filtration, solvent was removed under pressure and degradation products were analyzed by SEC.
- For the degradation with TBD and iPrNH₂, the degraded polymer was directly analyzed by SEC

Degradation of Copo1-Copo2:
In a 5 mL vial, 15 mg of polymer copolymer was dissolved in 0.750 mL of THF. After solubilization, 0.750 mL of KOH 5 wt% in MeOH was added. The cloudy mixture was stirred...
at room temperature during 96 h. Sample was dried under vacuum, then 1.5mL of chloroform were added. Salts were removed by filtration, solvent was removed under pressure and degradation products were analyzed by SEC.

Degradation of Copo3:

In a 5 mL vial, 15 mg of copolymer was dissolved in 0.750 mL of THF. After solubilization, 0.750 mL of degradation solution (KOH 5 wt% in MeOH or DBU 2.5 wt% in THF or TBD 2.5 wt% in THF) was added. The cloudy mixture was stirred at room temperature during 17h for KOH and DBU degradation and 1h for TBD degradation. Sample was dried under vacuum:

- For the degradation with KOH, 1.5 mL of chloroform were added. Salts were removed by filtration, solvent was removed under pressure and degradation products were analyzed by SEC.
- For the degradation with DBU, the degraded polymer was directly analyzed by SEC.
- For the degradation with TBD, 5 mL de dichloromethane was added then wash twice with water, then dried with MgSO₄, concentrated under pressure and analyzed by SEC.

Figure S5: Degradation of reference PS: PS2 (blue line), KOH degradation (light blue line), PS1 (green line), KOH degradation (light green line), PS3 (red line), KOH degradation (brown line), TBD degradation (magenta line), DBU degradation (orange line), TFA degradation (purple line) and APTS degradation (pink line).
**Figure S6:** Kinetic of degradation of **Copo3** in KOH: Copo3 (black line), 1h of degradation (green line), 4h of degradation (blue line) and 18h of degradation (red line).

**Figure S7:** Degradation by aminolysis of **Copo3**: Copo3 (black line) and degradation with iPrNH₂ (red line, $M_n = 72000$ g.mol⁻¹).
**b. Bacterial degradation**

In order to investigate the bacterial degradation of the polystyrene samples, we first optimized the reaction volume and concentration of bacteria that will enable to have a signal by microcalorimetry. This preliminary study was performed using both *P. aeruginosa* and *A. niger* with a medium culture that contain carbon. We obtained an increase of the total main heat when 100 μL and a concentration of bacteria equals to 0.25 - 0.5 McFarland was used.

For the bacterial degradation of polystyrene, we thus used a reaction medium without carbon to force the bacteria to use PS as a feed. The medium that was used is K$_2$HPO$_4$ (0.5 g/L), KH$_2$PO$_4$ (0.5 g/L), CaCl$_2$ (0.05 g/L), KCl (0.05 g/L), NaCl (5 g/L) in sterilized distilled water.

The bacterial degradation was then performed by adding P(S-co-DOT) **Copo3** or **PS3** as a powder to this medium and thus inserted into the microcalorimeter. The analysis was performed during 70 hrs. The results are then presented on the following figure:
Figure S9: Total main heat (μJ) observed by microcalorimetry for the bacterial degradation of copo3 and PS3.

These preliminary results showed premises for the bacterial degradation of polystyrene containing thioester linkages.

c. Time-resolved degradation

Time-resolved measurement of polymer degradation were performed with a MARS 60 rheometer (Thermo Scientific) using a Peltier cell equipped with 16 mm concentric cylinder geometries. Evaporation of solvents during the experiment was completely prevented by using an insulated hood and integrated solvent traps filled with low viscosity paraffin oil. The polymer solutions (20 wt% in THF, 4.3 mL) were first equilibrated at 25°C and viscosities were measured by applying a low shear stress of 0.1 Pa, that is within the Newtonian domain (the corresponding shear rates are lower than 5 s⁻¹). All measures are averaged over 30 s to improve the sensitivity in such low-torque conditions. The specific viscosities are obtained as following: \( \eta_{sp} = \frac{\eta_{solution}}{\eta_{solvent}} \), after measuring the viscosity of pure THF in the same conditions (\( \eta_{solvent} = 0.48 \) mPa.s).

After equilibration, concentrated TBD solutions in THF (1 mL, 6.6 wt%) were added in the cell and thorough mixing was applied to ensure proper mixing (shear rate = 200 s⁻¹ for 30 s). The corresponding TBD concentration after dilution is thus 1.25 wt%. Subsequently the viscosities were monitored using the previous method until stabilization, up to 2h for copo3.
7. Cross-linked material

a. Procedure

In a 10mL vial, fitted with a rubber septum, a mixture of divinylbenzene (12.6 mg, 9.7 x 10^-5 mol), and styrene (1 g, 9.6 x 10^-3 mol) was degassed with argon. The mixture was then immersed in a preheated oil bath at 150 °C during 2h.

In a 10mL vial, fitted with a rubber septum, a mixture of divinylbenzene (13.3 mg, 1.02 x 10^-4 mol), DOT (115.5 mg, 5.1 x 10^-4 mol), and styrene (1 g, 9.6 x 10^-3 mol) was degassed with argon. The mixture was then immersed in a preheated oil bath at 150°C during 2h.

b. Degradation

Pellets were immersed in a 5 mL of THF and 5 mL of a solution of KOH 5 wt% in MeOH or 2.5 wt% of TBD in THF.

8. Triggered degradation

a. Synthesis of photolatent TBD

TBD (0.999 mol, 1.39g) and PA (1.5 g, 0.999 mol) were dissolved in chloroform (40 mL). The mixture was stirred overnight at room temperature, and then the solvent was evaporated. The resulting compound was further purified by recrystallization twice from diethyl ether. Yield : 95 %.
b. Degradation in solution

A solution of photolatent TBD in THF was prepared (4wt% : 200 mg photolatent TBD + 4.8 g THF). The solution was put in ultrasonic bath for 1h, then stirred overnight at rt. Since the photolatent TBD was not entirely soluble, the excess photolatent TBD was eliminated by filtration on 0.45 µm filter. For maximum solubility, the solution was lightly heated with a heat-gun just prior to the filtration.

15 mg of Copo 3 was dissolved in 0.75 mL of THF and then added to 0.75 mL of the degradation solution in a small tube. The obtained solution was irradiated for 25 min at 254 nm (using a Hamamatsu LC8 at 50 % intensity) and stirred manually every 2min30. The tube was then capped and left for 1h30 at rt. The THF was evaporated and the remaining was dissolved in 4 mL of SEC-THF elution solvent, that was filtered on 0.45 µm PTFE filter and finally analyzed by SEC-THF.

9. Calculation details

All the calculations were performed using the Gaussian 16 package. The geometry of all species was optimized at the (U)B3LYP/6-31G(d) level of theory. Vibrational frequencies were calculated to ensure, that the obtained geometries were minima or transition states (0 or 1 imaginary frequency respectively) and to determine enthalpy values (standard frequency scale factor value 0.9603 was used). Intrinsic reaction coordinate (IRC) calculations, at the same level of theory, were performed to ensure that the transition states led to the expected reactants and products.
DOT

C  0.011375  0.068445  0.028566
C  0.003400  0.011503  1.434416
C  1.252247 -0.040568  2.112605
C  2.440057 -0.037502  1.357342
C  2.418996 -0.003659 -0.030536
C  1.194833  0.055933 -0.700105
H  -0.939090  0.094140 -0.495520
H  3.384521 -0.055562  1.889126
H  3.351986 -0.019703 -0.586282
H  1.161636  0.084262 -1.785738
C  -1.307491  0.020707  2.131082
C  -2.363939  0.824459  1.674707
C  -1.531866 -0.819294  3.240065
C  -3.611760  0.786675  2.294432
H  -2.197771  1.501176  0.841781
H  -2.783875 -0.851553  3.856878
C  -3.828375 -0.057485  3.384551
H  -4.412799  1.423648  1.929684
H  -2.938991 -1.503623  4.712964
H  -4.799324 -0.088777  3.870497
C  1.397220  0.000832  3.599679
C  -0.384489 -1.635611  3.753504
H  0.093538 -2.225632  2.963262
H  -0.687251 -2.301427  4.562878
O  0.606805 -0.769221  4.361058
S  2.510642  0.953930  4.363139

Sum of electronic and thermal Enthalpies = -1012.713172 Hartree
Sum of electronic and thermal Enthalpies = -310.087212 Hartree

\langle S^2 \rangle = 0.779888

radMA

\begin{array}{ccc}
C & -0.002821 & -0.000013 \quad -0.006822 \\
C & 0.001549 & 0.000158 \quad 1.393999 \\
C & 1.197624 & 0.000200 \quad 2.098087 \\
C & 2.450326 & -0.000095 \quad -0.006328 \\
C & 1.216562 & -0.000133 \quad -0.699454 \\
H & -0.942688 & -0.000065 \quad -0.551694 \\
H & -0.940559 & 0.000268 \quad 1.936740 \\
H & 1.180812 & 0.000323 \quad 3.183949 \\
H & 3.358767 & -0.000187 \quad -0.549515 \\
H & 1.221775 & -0.000253 \quad -1.786576 \\
C & 3.689527 & 0.000112 \quad 2.103964 \\
H & 4.593538 & -0.000024 \quad 1.499483 \\
C & 3.841900 & 0.000367 \quad 3.593233 \\
H & 3.373068 & -0.880064 \quad 4.058729 \\
H & 4.896903 & 0.000275 \quad 3.882139 \\
H & 3.373312 & 0.881110 \quad 4.058386 \\
\end{array}
Sum of electronic and thermal Enthalpies = -306.937217 Hartree

$<S^2>=0.756686$

DOT_STY_add_ea

\[
\begin{align*}
&\text{C} & 0.007116 & -0.003401 & 0.019440 \\
&\text{C} & 0.011804 & 0.055436 & 1.427070 \\
&\text{C} & 1.335158 & 0.092695 & 2.130494 \\
&\text{C} & 1.274738 & -0.136675 & -0.742902 \\
&\text{C} & 2.474060 & 0.571296 & -0.423244 \\
&\text{C} & 2.595088 & 1.557776 & 0.670892 \\
&\text{H} & 1.989880 & -0.731530 & 1.821739 \\
&\text{H} & 1.215836 & 0.063459 & 3.215335 \\
&\text{C} & 3.600671 & 0.388283 & -1.257550 \\
&\text{C} & 3.575989 & -0.467621 & -2.348327 \\
&\text{H} & 4.502935 & 0.944053 & -1.028056 \\
&\text{C} & 2.406569 & -1.169157 & -2.653321 \\
&\text{H} & 4.467918 & -0.590770 & -2.956261 \\
&\text{C} & 1.280207 & -0.994051 & -1.858017 \\
&\text{H} & 2.373789 & -1.850464 & -3.498964 \\
&\text{H} & 0.376147 & -1.550718 & -2.085663 \\
&\text{C} & -1.230922 & 0.020053 & -0.643867 \\
&\text{C} & -2.427307 & 0.083676 & 0.068166 \\
&\text{H} & -1.253035 & 0.011684 & -1.729512 \\
&\text{C} & -2.411925 & 0.126316 & 1.462924 \\
&\text{H} & -3.371744 & 0.108568 & -0.468660 \\
&\text{C} & -1.189880 & 0.119908 & 2.134648 \\
&\text{H} & -3.341943 & 0.177211 & 2.022032 \\
&\text{H} & -1.165067 & 0.166080 & 3.220877 \\
&\text{S} & 3.490995 & 2.967575 & 0.532427 \\
&\text{O} & 1.999281 & 1.347980 & 1.873594 \\
&\text{C} & 5.587473 & 2.743990 & 1.801438 \\
&\text{H} & 5.370581 & 3.678843 & 2.311160 \\
&\text{C} & 5.342202 & 1.502084 & 2.610071 \\
&\text{H} & 5.178538 & 0.620352 & 1.979534 \\
&\text{H} & 6.205414 & 1.282005 & 3.257298 \\
&\text{H} & 4.460839 & 1.622962 & 3.244204 \\
&\text{C} & 6.626224 & 2.822563 & 0.796767 \\
&\text{C} & 7.039936 & 4.086357 & 0.310204 \\
&\text{C} & 7.258081 & 1.676070 & 0.258214 \\
&\text{C} & 8.027274 & 4.198214 & -0.660152 \\
\end{align*}
\]
Sum of electronic and thermal Enthalpies = \(-1322.791176\) Hartree

Imaginary frequency = \(i243\) cm\(^{-1}\)

\(<S^2> = 0.789864\)

**DOT_MA_add_ea**
Sum of electronic and thermal Enthalpies = -1319.649420 Hartree

Imaginary frequency = i229 cm⁻¹

<\textit{S}²> = 0.778194

\textbf{DOT\_STY\_ouv}

\begin{verbatim}
C  0.129141 -0.183424  0.385854
C  0.318240 -0.257436  1.810279
C  1.580105 -0.146102  2.419237
C  1.290125 -0.106037 -0.548976
C  1.499060  0.980873 -1.431268
C  0.652930  2.215069 -1.333853
H  2.481762  0.036063  1.848423
H  1.673010 -0.207211  3.498745
C  2.551113  0.939479 -2.358744
C  3.412243 -0.153541 -2.415220
C  2.708768  1.786388 -3.019163
C  3.219785 -1.224807 -1.543402
H  4.229433 -0.163890 -3.130704
C  2.168109 -1.197471 -0.628156
H  3.881038 -2.086430 -1.579329
H  2.005468 -2.043046  0.033776
C -1.160331 -0.251708 -0.139904
C -2.281021 -0.403343  0.682109
H -1.290720 -0.200127 -1.217973
C -2.114018 -0.493177  2.071416
H -3.272365 -0.460176  0.241840
C -0.846516 -0.423157  2.620143
H -2.978962 -0.616099  2.717953
H -0.715929 -0.482153  3.697915
S  0.192710  2.924998 -2.937098
\end{verbatim}
O  0.286535  2.698689  -0.282626  
C  -0.719273  4.441568  -2.349105  
H  -1.254693  4.098724  -1.459701  
C  0.255696  5.550611  -1.938631  
H  -0.308112  6.421068  -1.581972  
H  0.901565  5.203228  -1.128059  
C  -1.713947  4.847577  -3.417794  
C  -3.085554  4.662553  -3.201057  
C  -4.020794  5.042628  -4.164312  
H  -3.422154  4.218186  -2.267255  
C  -2.231222  5.794807  -5.596552  
H  -0.239613  5.565690  -4.823108  
C  -3.595976  5.610156  -5.366262  
H  -5.080718  4.894661  -3.974797  
H  -1.890804  6.233554  -6.530843  
H  -4.322210  5.906329  -6.118449  

Sum of electronic and thermal Enthalpies = -1322.8147 Hartree

<S^2>=0.784185

**DOT_MA_ouv**

C  0.094396  0.595833  -0.323615  
C  -0.021681  0.333241  1.051862  
C  1.106161  0.006958  1.886798  
C  2.505485  0.063082  1.375444  
C  3.006596  -2.407026  1.912524  
C  3.399857  -1.025143  1.477558  
H  1.041241  0.538597  -0.845275  
H  -0.787537  0.831844  -0.910191  
O  3.615655  -3.024332  2.761661  
S  1.668896  -3.129176  0.930641  
C  1.525658  -4.786058  1.745272  
H  2.315653  -4.772911  2.503638  
C  3.009248  1.282867  0.890383  
C  4.345900  1.427360  0.527720  
H  2.337709  2.133931  0.828722  
C  5.227424  0.352670  0.663487  
H  4.703337  2.384986  0.158936  
C  4.754303  -0.862635  1.146190  
H  6.274931  0.461767  0.397560
Sum of electronic and thermal Enthalpies = -1319.670521 Hartree

\(<S^2>=0.784155\)

HomoDOT

```plaintext
C  -2.422502  0.332754  -2.616495
C  -2.905365  0.235336  -1.305123
C  -3.031293  1.426330  -0.549252
C  -2.678113  2.657874  -1.122310
C  -2.210434  2.730385  -2.431813
C  -2.080902  1.562133  -3.180412
H  -2.305469  -0.578945  -3.194481
H  -2.800794  3.567581  -0.543345
H  -1.953678  3.693733  -2.862804
H  -1.711143  1.602732  -4.201244
C  -3.580540  1.387104  0.841800
S  -2.796205  2.583703  1.975809
C  -3.789236  2.281768  3.477345
```
H  -3.118474  2.075241  4.313648
H  -4.406452  3.154407  3.701091
H  -4.422903  1.413370  3.277740
O  -4.449610  0.622603  1.210786
C  -3.258442 -1.124982  0.784917
C  -4.440528 -1.725285  1.239304
C  -2.419589 -1.837884  0.097382
C  -4.804908 -3.005603  0.828308
H  -5.085466 -1.168055  1.912999
C  -2.795388 -3.126112  0.499765
C  -3.980768 -3.710085  0.049353
H  -5.730369 -3.446984 -1.188073
H  -2.149190 -3.676412  1.175851
H  -4.254314 -4.708332  0.380005
C  -1.109145 -1.280492  0.586431
H  -1.085813 -0.191657  0.593614
H  -0.879980 -1.647578  1.590322
S   0.268268 -1.841012 -0.549940
C   1.637851 -0.915873  0.056448
C   2.927565 -1.493895  0.285300
C   4.179277 -0.767352  0.254019
C   2.164708  1.176375  1.099961
C   4.314099  0.674908 -0.076467
C   3.388275  1.640736  0.371086
H   2.409387  0.566174  1.978174
H   1.538702  2.015160  1.412612
O   1.333439  0.401417  0.210014
C   2.997342 -2.901617  0.526699
C   4.189669 -3.558071  0.756908
H   2.068773 -3.460160  0.543806
C   5.394585 -2.842199  0.766470
H   4.183505 -4.627538  0.950578
C   5.365151 -1.474601  0.516104
H   6.337658 -3.340166  0.971605
H   6.297129 -0.917816  0.537945
C   5.416480  1.126184 -0.826643
C   5.609225  2.479628 -1.095353
H   6.118878  0.400642 -1.224933
C   4.697071  3.425348 -0.626501
H   6.468644  2.792792 -1.682333
C   3.584442  2.994985  0.095450
H   4.840243  4.481961 -0.834624
H   2.853961  3.717866  0.451792

Sum of electronic and thermal Enthalpies = -2065.284169 Hartree

<\text{S}^2>=0.773099

\text{HomoDOT}_{\text{ea}}
Sum of electronic and thermal Enthalpies = -2065.267075 Hartree

Imaginary frequency = 1236 cm⁻¹

<S²> = 0.792601

Rad-DOT
Sum of electronic and thermal Enthalpies = -1052.562452 Hartree

\[ <S^2> = 0.78418 \]

**HomoDOT-ouv_conf1**

C     1.468189     2.058080     -0.818224
C     2.295384     1.110582     -0.199912
C     3.474744     0.710728     -0.872799
C     3.789229     1.264644     -2.123458
C     2.959264     2.215262     -2.712645
C     1.794262     2.610750     -2.057598
H     0.551095     2.353954     -0.317381
H     4.705421     0.964506     -2.621986
H     3.224652     2.643845     -3.674812
H     1.134497     3.346886     -2.509028
C     4.410532     0.275204     -0.245085
S     5.103696     -1.472989     -1.431050
C     6.211527     -2.405143     -0.319163
H     5.984929     -3.470010     -0.400250
H     7.253835     -2.232678     -0.589671
H     6.019505     -2.054268     0.698452
O     4.672521     -0.307060     0.937226
C     1.873009     0.563115     1.130637
C     2.159280     1.301895     2.285611
C 1.144273 -0.639112  1.241846
C 1.742197  0.865061  3.541165
H 2.729004  2.220888  2.191859
C 0.731363 -1.068045  2.511987
C 1.026162 -0.327005  3.654280
H 1.983335  1.448999  4.425459
H 0.162229 -1.989327  2.591169
H 0.700324 -0.681846  4.628565
C 0.781482 -1.471424  0.035816
H 1.545407 -1.436720 -0.743185
H 0.611995 -2.513021  0.315803
S -0.773197 -0.923469 -0.813522
C -1.982224 -1.880697  0.110082
C -3.411337 -1.645319 -0.292221
C -4.033495 -0.377256 -0.335659
C -3.633985  2.099791  1.978942
C -3.381052  0.859410  0.180659
C -3.261426  2.048012 -0.624994
H -4.005172  1.233315 -2.510928
H -3.521440  3.021927 -2.540131
O -1.675158 -2.734230  0.922133
C -4.133765 -2.798353 -0.637498
C -5.450837 -2.710998 -1.075017
H -3.638023 -3.761635 -0.568231
C -6.067892 -1.460346 -1.147753
H -5.993012 -3.610422 -1.352725
C -5.369144 -0.316078 -0.772084
H -7.099983 -1.377272 -1.477632
H -5.867220  0.648704 -0.785013
C -2.916515  0.876145  1.497060
C -2.343515  2.018534  2.061948
H -3.013073 -0.024073  2.097874
C -2.240320  3.190998  1.298592
H -1.983887  1.993874  3.085985
C -2.691696  3.205115 -0.009045
H -1.807307  4.088210  1.733097
H -2.606148  4.110974 -0.604525

Sum of electronic and thermal Enthalpies = -2065.293225 Hartree

<S^2>=0.784186

HomoDOT-ouv_ea
C -3.910385 1.540206 -1.296748
H -3.282415 -0.249280 -2.382153
H -2.475245 1.306495 -2.909782
O -1.701784 0.361250 -0.865139
C -3.184453 -2.637120 0.600767
C -4.340186 -3.217863 1.083241
H -2.280705 -3.236481 0.570886
H -3.282415 -0.249280 -2.382153
C -5.519868 -4.637778 1.232411
H -4.331093 -4.252534 1.413988
C -5.498297 -4.154943 0.696854
H -6.448860 -2.906047 1.472201
H -6.425453 -0.581721 0.703529
C -5.312839 1.739116 0.666766
C -5.522710 3.086940 0.397432
H -5.745288 1.310786 1.565638
C -4.916759 3.684052 -0.715581
H -6.138474 3.673030 1.068752
C -4.108817 2.915629 -1.538360
H -5.066203 4.739684 -0.924367
H -3.621290 3.365893 -2.399810

Sum of electronic and thermal Enthalpies = -2065.26167 Hartree
Imaginary frequency = i598 cm⁻¹
<S²> = 0.764464

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