# Supporting Information: Capturing free-radical polymerization by synergetic *ab-initio* calculations and topological reactive molecular dynamics

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Extra details on the TraPPE-UA force field; Templates used in the matching topology algorithm.

## TraPPE-UA Force Field

The TraPPE-UA[1–6] force fields parameters were obtained by site *http* : *//trappe.oit.umn.edu*. In the tables are listed all force field parameters.

Table S1: Not bonded interaction parameters $v_{NB}(r_{ij}) = 4\epsilon_{ij}[(\frac{r_{ij}}{\sigma_{ij}})^{12} - (\frac{r_{ij}}{\sigma_{ij}})^{6}] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$; $\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj})$; $\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}$

| ID | Atom | $\epsilon/k_B(K)$ | $\sigma$(Å) | q(e) |
|---|---|---|---|---|
| 1 | $[CH_2]$=$CH_x$ | 85.0 | 3.675 | 0.0 |
| 2 | $CH_x$=[C]($sp^2$)-$CH_y$($sp^2$) | 22.0 | 3.850 | 0.0 |
| 3 | $CH_x$-O-[C]=O | 40.0 | 3.820 | 0.4 |
| 4 | $CH_x$-[O]-C=O | 55.0 | 2.800 | -0.25 |
| 5 | $CH_x$-$[CH_2]$-O-$CH_y$ | 46.0 | 3.95 | 0.25 |
| 6 | $CH_x$-$[CH_2]$-$CH_x$ | 46.0 | 3.95 | 0.0 |
| 7 | $CH_x$-O-C=[O] | 79.0 | 3.050 | -0.4 |
| 8 | $[CH_3]$-$CH_x$ | 98.0 | 3.75 | 0.0 |

Table S2: Bonds interaction parameters: $U_B(r_{ij}) = K(r_{ij} - r_0)^2$

| ID | Atom | $r_0$(Å) | k(kcal/mol) |
|---|---|---|---|
| 1 | $CH_x$=$CH_y$ | 1.33 | 300 |
| 2 | $CH_x$($sp^2$)-($CH_y$=O) | 1.52 | 300 |
| 3 | O-(C=O) | 1.344 | 300 |
| 4 | $CH_x$-O | 1.41 | 300 |
| 5 | $CH_x$-$CH_y$ | 1.54 | 300 |
| 6 | OC=O | 1.2 | 300 |

Table S3: Bending interaction parameters: $U_{bend}(\theta) = \frac{k_\theta}{2}(\theta - \theta_0)^2$

| ID | Atom | $\theta_0$(deg) | $k_\theta$ (K/rad$^2$) |
|---|---|---|---|
| 1 | $CH_x$=(C)-$CH_y$ | 119.7 | 70420 |
| 2 | O-(C)[=O]-$CH_x$, | 110.0 | 70600 |
| 3 | O=(C)[-$OCH_x$]-$CH_x$ | 125.0 | 62500 |
| 4 | C[=O]-(O)-$CH_x$ | 115.0 | 62500 |
| 5 | $CH_x$-($CH_y$)-O | 112.0 | 50300 |
| 6 | $CH_x$-($CH_2$)-$CH_y$ | 114.0 | 62500 |

Table S4: Dihedral parameters for $U^1_{tor}(\phi) = c_0 + c_1 cos(\phi) + c_2 cos(2\phi) + c_3 cos(3\phi) + c_4 cos(4\phi)$

| ID | Atom | $c_0/k_B$ | $c_1/k_B$ | $c_2/k_B$ | $c_3/k_B$ | $c_4/k_B$ (K) |
|---|---|---|---|---|---|---|
| 1 | $CH_2$=(C)-(C)[=O]-O | 823.03 | 47.91 | -773.13 | 1.99 | 0.00 |
| 2 | $CH_2$=(C)-(C)[-O]=O | 823.03 | -47.91 | -773.13 | -1.99 | 0.00 |
| 3 | $CH_x$-(O)-(C)($sp^2$)-C($sp^2$) | 1820.74 | 417.41 | -1373.14 | 30.19 | 0.00 |
| 4 | $CH_x$-(CH2)-(O)-C($sp^2$) | 2029.99 | -751.83 | -538.95 | -22.10 | -51.27 |
| 6 | O-(C)($sp^2$)-(C)($sp^2$)-$CH_3$ | 195.19 | 149.30 | 164.38 | -24.12 | 28.45 |
| 8 | $CH_x$-(O)-(C)=O | 1820.74 | -417.41 | -1373.14 | -30.19 | 0.00 |
| 9 | O=(C)-(C)($sp^2$)-$CH_3$ | 195.19 | -149.30 | 164.38 | 24.12 | 28.45 |

Table S5: Top table: dihedral parameters for $U^2_{tor}(\phi) = c_0 + c_1(1 + cos(\phi)) + c_2(1 - cos(2\phi)) + c_3(1 + cos(3\phi))$. Bottom table: dihedral parameters for $U^3_{tor}(\phi) = \sum_{n=1}^{4} A_n cos^{n-1}(\phi)$

| Id | Atom | $c_0/k_B$ | $c_1/k_B$ | $c_2/k_B$ | $c_3/k_B$ (K) |
|---|---|---|---|---|---|
| 5 | $CH_x$-($CH_2$)-($CH_2$)-O | 0.00 | 176.62 | -53.34 | 769.93 |
| 7 | $CH_x$-($CH_2$)-($CH_2$)-$CH_y$ | 0.00 | 355.03 | -68.19 | 791.32 |
| 10 | $CH_x$-($CH_2$)-(C)=O | 2035.58 | -736.90 | 57.84 | -293.23 |

| ID | Atom | $A_1/k_B$ | $A_2/k_B$ | $A_3/k_B$ | $A_4/k_B$ (K) |
|---|---|---|---|---|---|
| 11 | $CH_x$-$CH_2$-C(=O)-O | 373.05 | 919.04 | 268.15 | 1737.21 |

# Templates used in the matching topology algorithm

In the templates files a certain number of atoms can represent the "edges" of the reaction whose close atoms topology does not need to be updated. In particular, in each HDDMA monomer, two half monomers are available to react since each half monomer contains a reactive (-CH=$CH_2$) vinyl group, while the edge points are represented by the most peripherals atoms with respect to the vinyl units. In the following, three templates are needed to allow the reaction to proceed. The details of the three templates are reported in Figures S1 and S2.

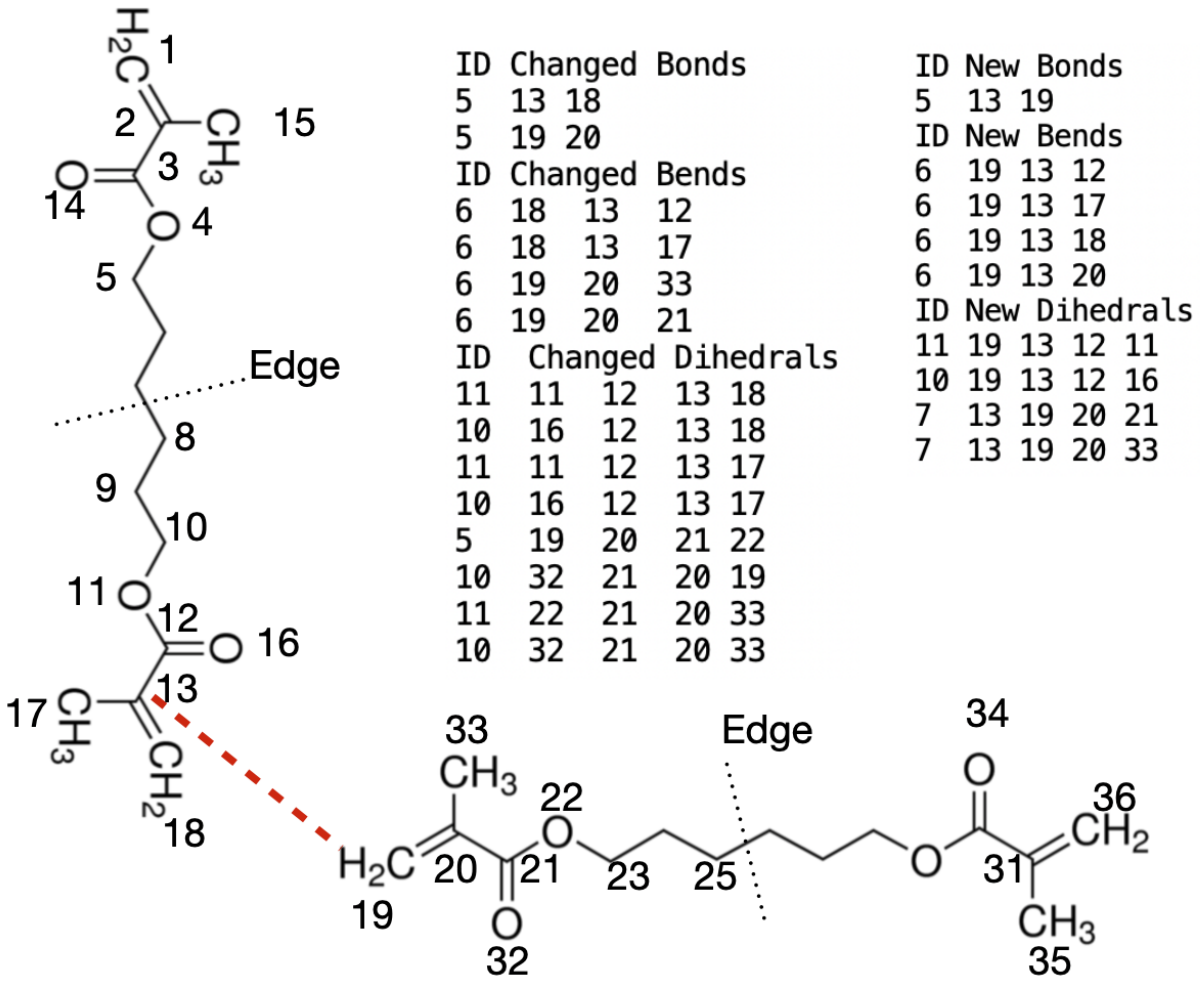


Figure S1: Edges are represented by black dotted line and between the two reacting carbons a red dotted line is present. Topology changes done in the reaction of two monomers.

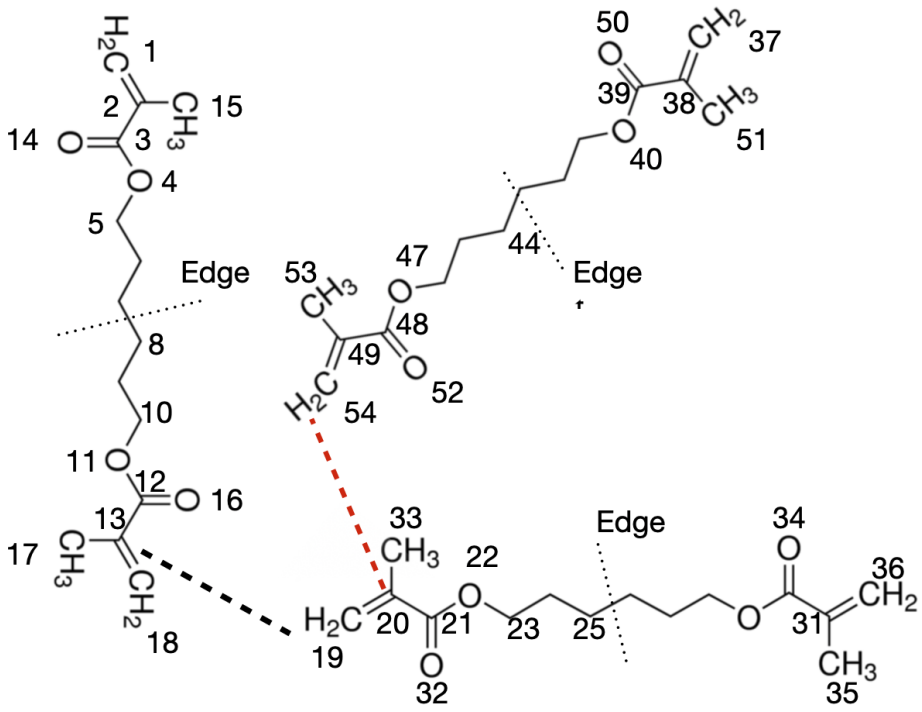


Figure S2: Edges are represented by black dotted line and between the two reacting carbons a red dotted line is present. Topology changes done in the reaction of one monomer with a just reacted monomer.

# References


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