Supporting Information to accompany:

Modelling the free-radical polymerization of hexanediol diacrylate (HDDA): a molecular dynamics and graph theory approach

1

Force field

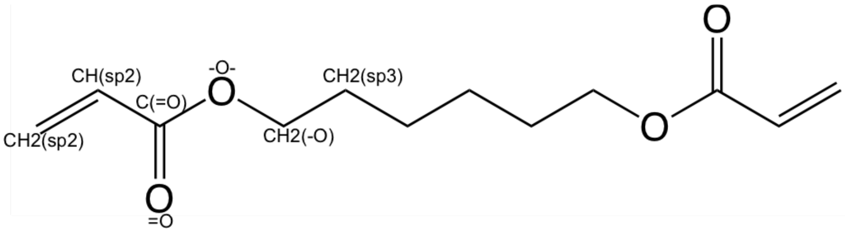


Table S1: *TraPPE-UA non-bonded interactions parameters. The non-bonded interactions are described with the pairwise-additive 12-6 Lennard-Jones (LJ) and Coulombic potentials. For the Lennard-Jones potential a hard cutoff at 14 Å with analytical tail corrections was used. For the Coulombic potential a cutoff of 14 Å was used, and the Ewald summation method with precision 1e-6 was used for the long range electrostatics. The non-bonded intramolecular interactions are only calculated for atoms separated by four or more bonds. Intramolecular Coulmbic interactions were also calculated for atoms separated by three bonds but reduced by the scaling factor 0.5. The Lorentz-Berthelot mixing rules were used. Parameters taken from Maerzke* et al *[1]*

atom	$\epsilon(k_B/T)$	$\sigma(\AA)$	charge (e^-)
CH2(sp2)	85.0	3.675	0.000
CH(sp2)	52.0	3.710	0.000
C(=O)	40.0	3.820	0.400
−O−	55.0	2.800	-0.250
CH2(−O)	46.0	3.950	0.250
CH2(sp3)	46.0	3.950	0.000
O=	79.0	3.050	-0.400

Table S2: *TraPPE-UA bonds parameters. In the TraPPE forcefield bonds are rigid. In this work, we modeled the bonds using a harmonic potential ($U_b = k_b(x - x_0)^2$) as otherwise the breaking of bonds is not possible. We took the value of the spring constant to be 300 kcal/mol for all bonds based on the average value of the spring constant in the OPLS[2] force field. The equilibrium bond lengths were taken from Maerzke* et al *[1]*

bond	r_0	k (kcal/mol)
CH2(sp2)=CH(sp2)	1.330	300
CH(sp2)−C(=O)	1.520	300
O−C(=O)	1.344	300
O−CH2(-O)	1.410	300
CH2(sp3)−CH2(sp3)	1.540	300
C(=O)=O	1.200	300

Table S3: *TraPPE-UA bends force field parameters.* $U_\theta = k_\theta(\theta - \theta_0)^2$. *Parameters taken from Maerzke* et al *[1] except for the one indicated with a *. This one was taken from [3]*

bend	angle (degrees)	k_θ (kcal/mol)
CH2(sp2)=CH(sp2)−C(=O)	119.7	69.962
CH(sp2)−C(=O)−O*	110.0	70.140
C(=O)−O−CH2(−O)	115.0	62.099
O−CH2−CH2*	111.0	35.07
CH2−CH2−CH2	114.0	62.099
CH(sp2)−C(=O)=O	126.0	40.04
O=C(=O)−O	123.0	40.04

Table S4: *TraPPE-UA dihedral force field parameters.* $U_{tor} = \sum_{n=0}^{4} k_n(cos(n\phi))$ *Parameters taken from Maerzke* et al *[1] except for the ones indicated with a *. These ones were taken from [4]*

dihedral	k_0 (kcal/mol)	k_1 (kcal/mol)	k_2 (kcal/mol)	k_3(kcal/mol)	k_4(kcal/mol)
CH2(sp2)=CH(sp2)−C(=O)−O	3.271	0.190	-3.072	0.007	0
CH(sp2)−C(=O)−O−CH2	7.236	1.658	-5.457	0.119	0
C(=O)−O−CH2(−O)−CH2	8.067	-2.988	-2.141	-0.087	-0.1018
O−CH2−CH2−CH2*	3.549	0.701	0.211	3.059	0
CH2−CH2−CH2−CH2*	4.2826	1.411	0.271	3.144	0
CH2(sp2)=CH(sp2)−C(=O)=O	3.271	-0.190	-3.072	-0.007	0
O=C(=O)−O−CH2(−O)	7.236	-1.658	-5.457	-0.119	0

2
HDDA network

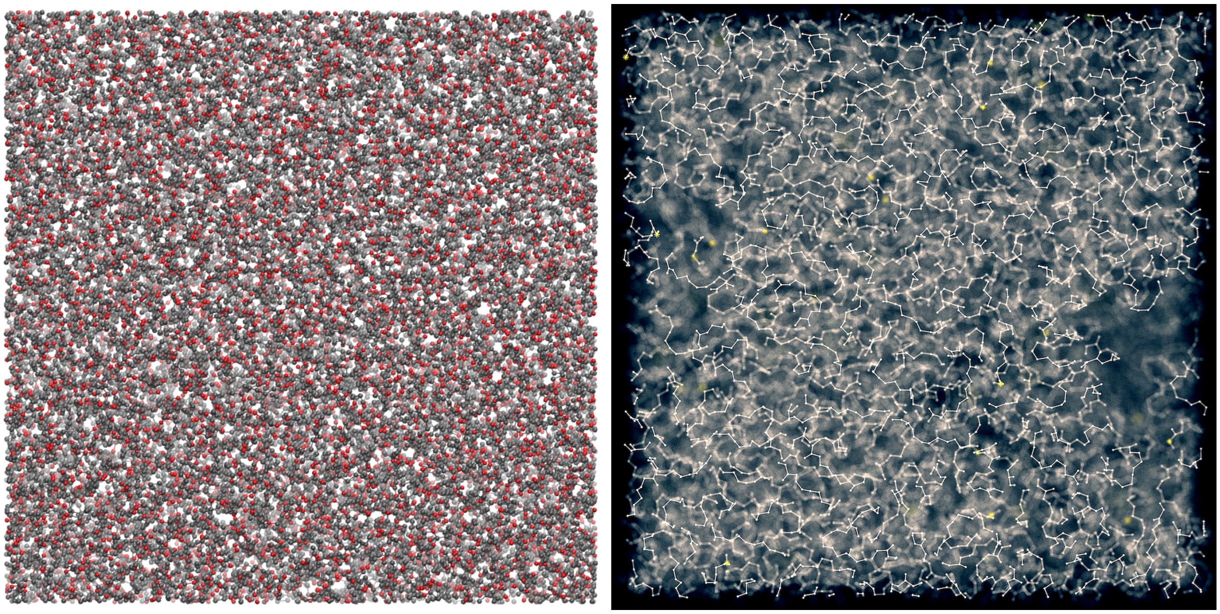


Figure S1: *Two different molecular representation of pHDDA. The simualtion box is periodic in every direction and has dimensions around 100×100 Å.*

3

Bond conversion

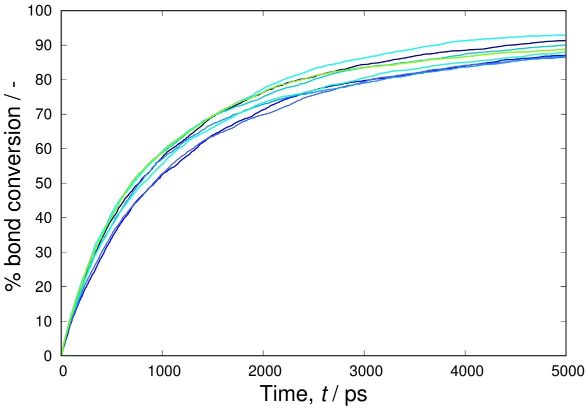


Figure S2: *Bond conversion evolution as a function of simulation time. The simulation time can not be directly compared with real time as the reactions are not explicitly modelled. Each color corresponds to a completely independent curing simulations. In the simulation methodology the number of radicals can only decrease, hence the initial autoacceleration of the polymerization process (due to the increasing concentration of radicals in the system) is not captured.*

4

Effect of curing temperature in the curing simulations

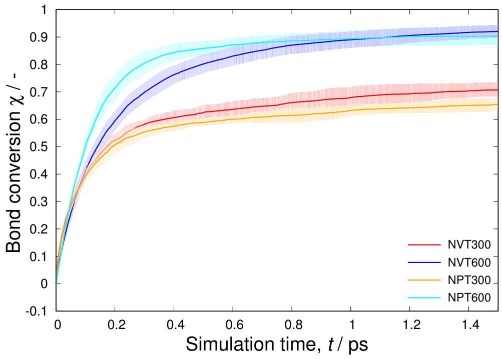


Figure S3: *The curing temperature has an effect on the speed of the reactions and on the end-conversion achieved. When the simulations are performed at 300 K, the overall mobility of the system is lower. This leads to (1) a slower conversion as a function of simulation time and (2) a lower end-conversion value. In order to achieve conversion values close to 85% at a curing temperature of 300 K very long simulations have to be performed. The curing ensemble appears to have a much less significant effect in the bond conversion. However, the NVT ensemble in general enables slightly higher conversion because the system does not suffer from volume shrinkage.*

5

Molecules flexibility and small cycles

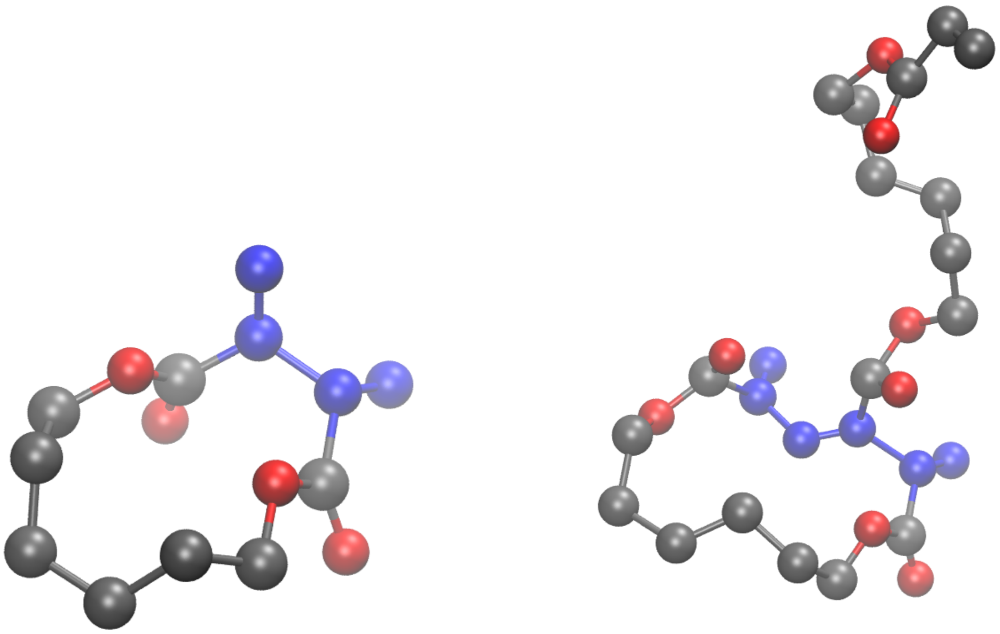


Figure S4: *Example of small cycles formed by one and two HDDA molecules via propagation. Color code: carbon=black, oxygen=red, carbons in vinyl group=blue*

6

Molecules flexibility and small cycles

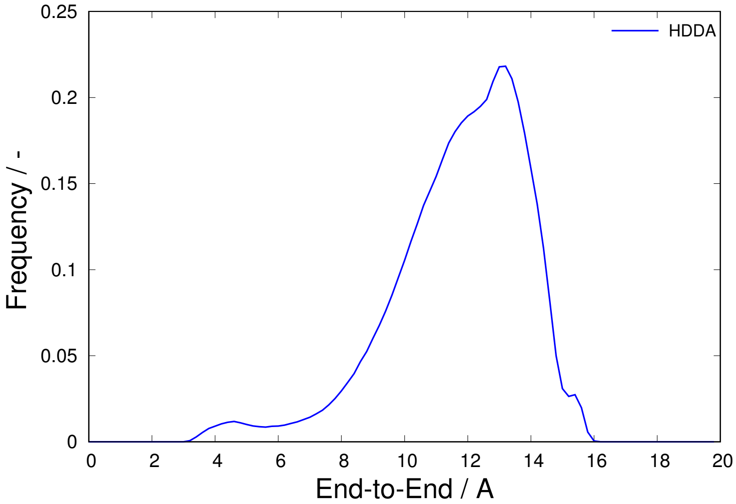


Figure S5: *Histogram of the end-to-end distance of HDDA molecules in the liquid phase at 300 K.*

7

Metadynamics: flexibility of HDDA

Metadynamics is a method aimed to enhance the sampling of separated regions in phase space and map out the underlying free energy landscape as a function of a small number of order parameters or collective variables (CVs) [5].

In this method, an external history-dependent bias potential is constructed in the space of a few collective variables $\vec{s}(q)$ to push the system away from local minima into exploring new regions of the CVs-space. The metadynamics potential is built as a sum of Gaussians deposited along the trajectory in the CVs space:

$$V(\vec{s},t) = \sum_{k\tau<t} W(k\tau)\exp(-\sum_{i=1}^{d}\frac{(s_i - s_i(q(k\tau)))^2}{2\sigma_i^2}). \tag{7.1}$$

where τ is the Gaussian deposition stride, σ_i the width of the Gaussian for the ith CV, W(kτ) the height of the Gaussian and s_i the CVs.

The addition of 'hills' to the landscape, discourages the system from coming back to states already visited an hence, it encourages the system to explore the full free energy landscape. In the long time limit, the modified free energy becomes a constant as a function of the collective variable and the free energy landscape can be recovered as the opposite of the sum of all Gaussians.

In this work, we used LAMMPS software [6] patched with the freely available PLUMED package (www.plumed.org) to perform the metadynamics runs. For this, two things are required:

1. an extra fix in the LAMMPS input: fix id all plumed plumedfile plumed.input outfile plumed.out
2. a plumed.input file with the parameters for the metadynamics runs: σ, τ, W($k\tau$) (Eq. 7.1).

In our work we were interested in the free energy barrier of coiling an uncoiling in the liquid phase. Therefore, we chose the end-to-end distance between the vinyl functional groups in a HDDA molecule as the CV. In the coiled state, this CV has a value close to 4 Å and in the uncoiled state it has a value around 15 Å.

We used the following metadynamics parameters in the plumed.input file:

METAD ARG=distance SIGMA=0.045 HEIGHT=0.05 PACE=100

To fully describe the transition from coiled to uncoiled, the local environment of each molecule has to be considered some how in the CVs. Finding a CV or a few CVs that capture all the changes in the local environment is a rather complicated topic and therefore an entire different area of expertise. Because in this work we were only interested in a rough estimation of the average free energy barrier, we overcame this problem by computing the metadynamics potential for 50 different molecules of HDDA and reporting the range of the free energy barrier we found (5-10 kcal/mol).

8

Effect of different amount of initial reactive monomers

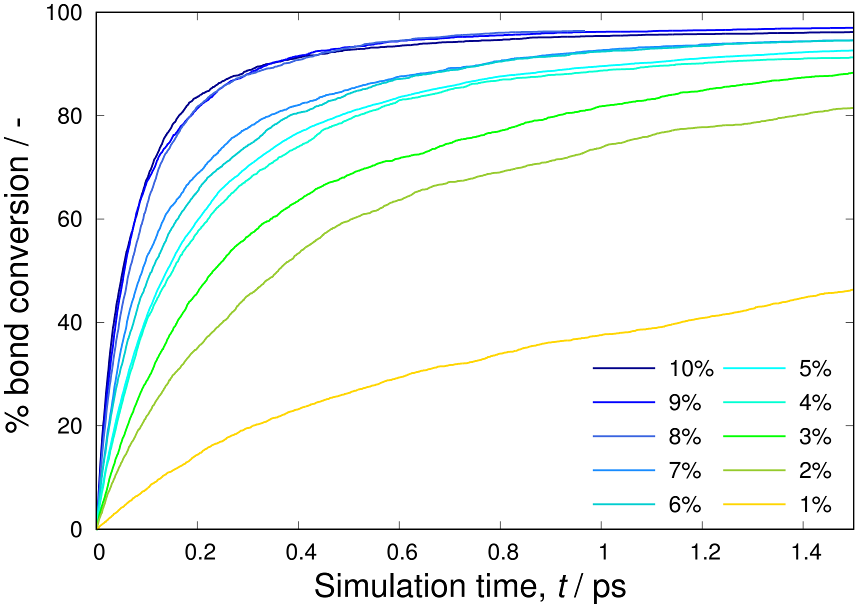
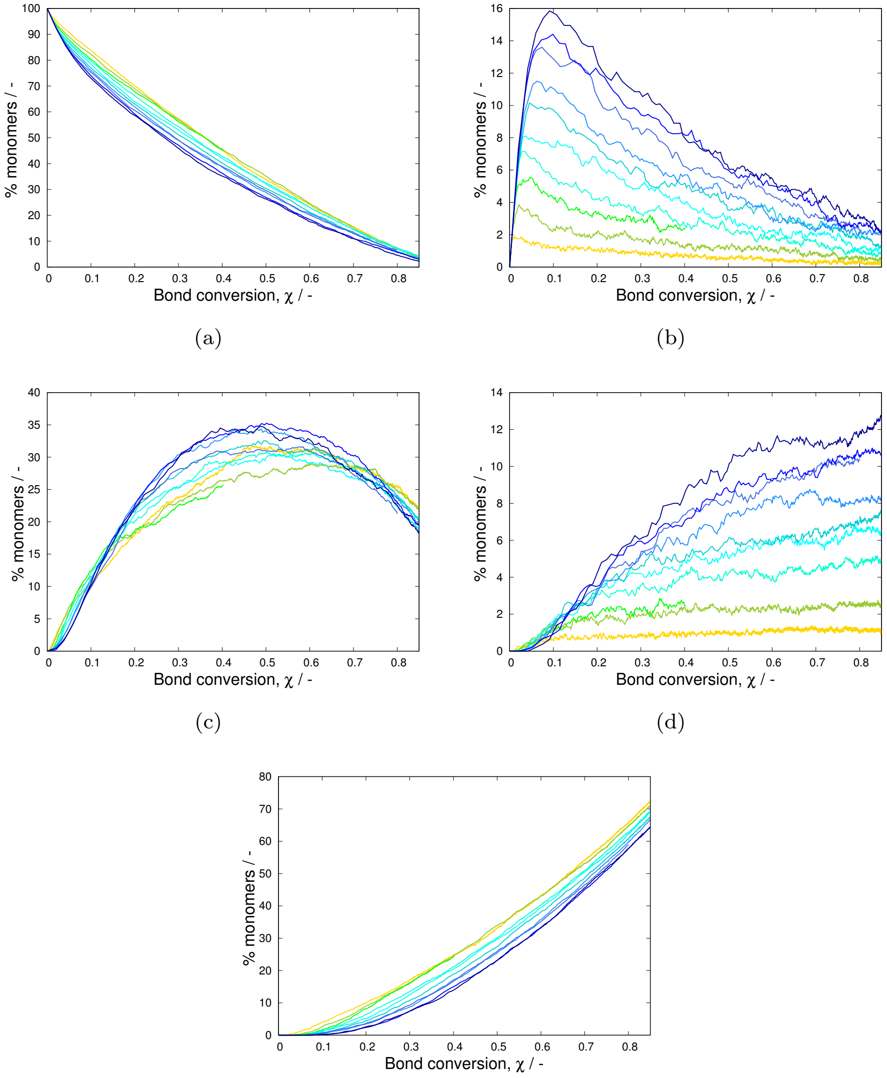


Figure S6: *Bond conversion for different concentrations of initial radical in the system.*



(a) (b) (c) (d) (e)

Figure S7: *Degree distributions for different concentrations of radicals. The dark blue line correspond to 10% radicals, the yellow to 1% radicals.(a) Degree zero, (b) degree one, (c) degree two, (d) degree three, (e) degree four.*

9

Elastic modulus calculations

$\boldsymbol{A}$ is a symmetric adjacency matrix: $A_{i,j} = 1$ if monomer i is connected to monomer j with a covalent bond, and $A_{i,j} = 0$ if no such connection exist. This matrix encodes essential information on the topology of the polymer network at a given point of time. For instance, for an arbitrary monomer i, $v_i = \sum_{i<j}^{n} A_{i,j}$ gives the number of neighbours this monomer is connected to. Degree distribution $d_k = \mathbb{P}[v_i = k]$ denotes the probability that a randomly chosen monomer has k neighbours. Although these two examples are seemingly simple, more perplexing properties of the polymer network can be extracted by performing various manipulations with the adjacency matrix. For example, the molecular size distribution $w(n)$ is given by the probability that the block-diagonalised version of $\boldsymbol{A}$ contains a block of size n. De Genes postulated that average resistance distance in the connectivity graph plays a definitive role in determining the elastic modulus of the corresponding material. The elastic modulus can be calculated from:

$$E = C \left(\frac{1}{n^2 - n} \sum_{i,j=1}^{n} (L^+_{i,i} + L^+_{j,j} - L^+_{i,j} - L^+_{j,i}) \right)^{-1},$$

where $\boldsymbol{L}^+$ is the Moore-Penrose inverse of the Laplacian matrix $\boldsymbol{L} = \mathrm{diag}\{\boldsymbol{v}\} - \boldsymbol{A}$.

Bibliography

[1] K. A. Maerzke, N. E. Schultz, R. B. Ross and J. I. Siepmann, *J. Phys. Chem. B*, 2009, **113**, 6415–6425.

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[4] J. M. Stubbs, J. J. Potoff and J. I. Siepmann, *J. Phys. Chem. B*, 2004, **108**, 17596–17605.

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