

Supporting Information for:
**PolySMart: a general coarse-grained molecular dynamics
polymerization scheme**

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S1-Homo-polymerization of lactic acid

The connectivity graphs for different conversion values of test case 1 (Homo-polymerization of lactic acid) are shown in Figure S1. These figures are generated with a code written in Matlab software utilizing the Matlab graph and network algorithm library. The program analyzes the connectivity of beads, identifies each chain, separates them for better visualization, and sorts them based on the number of their beads. This tool operates like size-exclusion chromatography and aids to have better visualization and quantitative measures of individual polymer chain molecular weights and the amount of residual short oligomers at different stages of the reaction. Given this information, we can analyze each individual chain in terms of length and shape and are able to calculate the molecular weight of each chain and so the dispersity index.

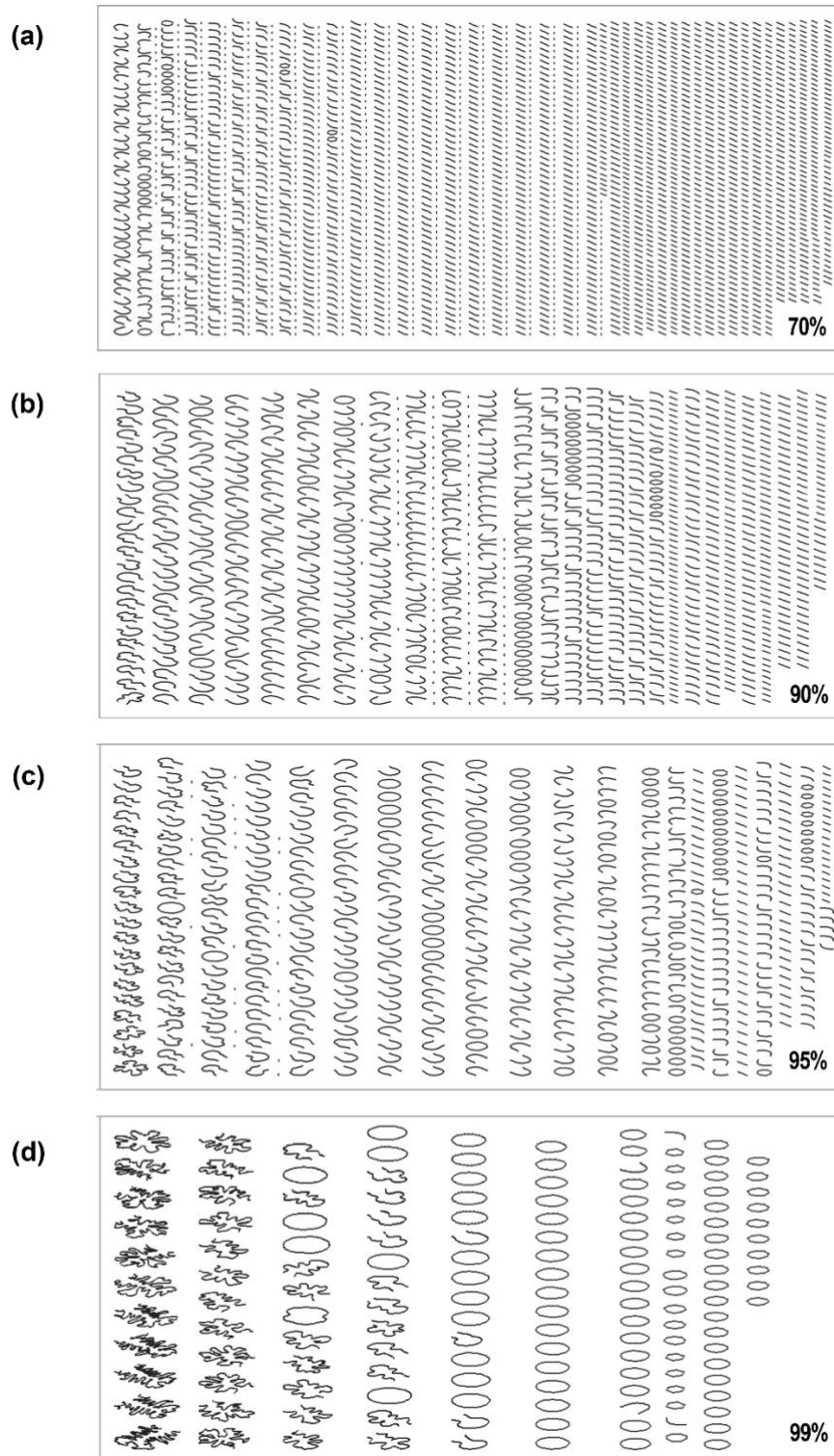


Figure S1. Structure of the formed PLA oligomers and chains at different conversion values. Topologies are made as simple graphs in which only the connectivity information of beads is considered and the correct positions of the beads in the simulation box are not preserved for better visualization.

S2- Bonded interaction parameters calculation

According to the recommended procedure for Martini3 CG forcefield, the following steps were done to determine the equilibrium values and force constants for bond and angle

potentials for all the molecules. First, a minimum of 5 ns *NPT* simulation was performed on a box containing at least 10 molecules, at the atomistic level by means of the OPLS-AA force field with a time step of 1 fs. Temperature and pressure were controlled using *v*-rescale thermostat and Parrinello-Rahman barostat. Thereafter the distributions of the bonds and angles connecting the center of the geometry (COG) of the atoms of a bead were averaged over time. The distributions were converted into potential values via equation S1. By fitting equations, S2 and S3, force constants for bonds, angles, and equilibrium values were obtained. A list of equilibrium values and force constants for all bonded interactions at the CG level is provided in Table S1-S9. For dendrimer, the dihedral potentials were also included, and the values were just manually set in a way that the dihedral potential distribution of the CG structure fits the atomistic distribution. For other cases, the dihedral potentials at the CG level were ignored for simplicity.

$$U = -\ln(p) kT \quad (S1)$$

$$U_{\text{bond}} = \frac{1}{2} K_{\text{bond}} (l - l_0)^2 \quad (S2)$$

$$U_{\text{angle}} = \frac{1}{2} K_{\text{angle}} [\cos(\theta) - \cos(\theta_0)]^2 \quad (S3)$$

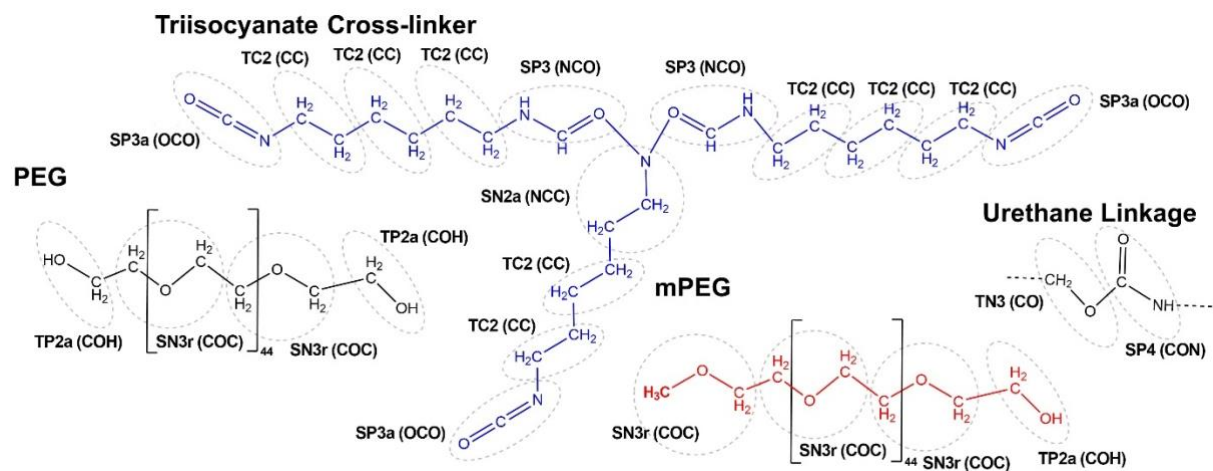


Figure S2. Martini CG model and bead types for crosslinked polyurethane network compositions.

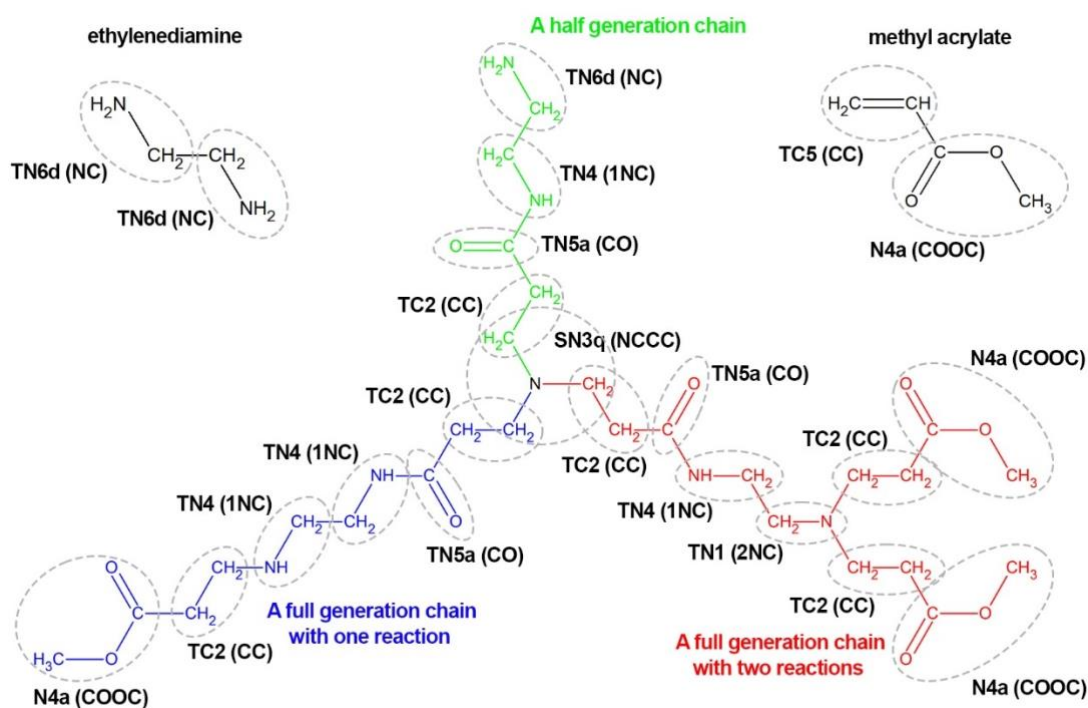


Figure S3. Martini CG model and bead types for monomers and dendrimer possible structures

Table S1. Bond type parameters for “homo-polymerization of lactic acid” case.

Bond	l_0 (nm)	K_{bond} (kJ mol ⁻¹ nm ⁻²)
lactic acid		
CCOH-COOH	0.268	30000
poly lactic acid		
CC-COO	0.282	33050
CCOH-COO	0.243	53300
CC-COOH	0.263	18000

Table S2. Bond type parameters for the “crosslinked polyurethane network” case.

Bond	l_0 (nm)	K_{bond} (kJ mol ⁻¹ nm ⁻²)
PEG and mPEG		
COH-COC	0.2692	11000
COC-COC	0.3119	7800
Triisocyanate Crosslinker		
OCO-CC	0.295	15500
CC-CC	0.248	32000
CC-NCO	0.278	16400
NCO-NCC	0.318	13600
NCC-CC	0.282	12500
Urethane Linkage		
CO-CON	0.290	30000

Table S3. Bond type parameters for the “PAMAM dendrimer” case.

Bond	l_0 (nm)	K_{bond} (kJ mol ⁻¹ nm ⁻²)
methyl acrylate		
CC-COOC	0.381	44000
ethylenediamine		
NC-NC	0.224	30000
dendrimer		
CC-NCCC	0.202	19600
CC-CO	0.217	46000
CO-1NC	0.262	53000
1NC-NC	0.248	13200
CC-1NC	0.258	14600
1NC-1NC	0.234	22900
1NC-2NC	0.227	40700
2NC-CC	0.268	11400
CC-COOC	0.348	24500

Table S4. Bond type parameters for “hyperbranched polymer” case.

Bond	l_0 (nm)	K_{bond} (kJ mol ⁻¹ nm ⁻²)
3, 5-dihydroxybenzoic acid		
CCR-COH	0.197	81531
CCR-COOH	0.287	176440
1, 6-dibromohexane		
CCA-CCB	0.284	38117
DMF		
CO-NCC	0.250	51746
Constraint		
l_0 (nm)		
3, 5-dihydroxybenzoic acid		
CCR-CCR	0.27	

Table S5. Angle type parameters for “homo-polymerization of lactic acid” case.

Angle	ϑ_0 (°)	K_{angle} (kJ mol ⁻¹ rad ⁻²)
polylactic acid		
CC-COO-CC	128.0	102
COO-CC-COO	68.0	217
CCOH-COO-CC	127.0	200
COOH-CC-COO	69.0	100

Table S6. Angle type parameters for the “crosslinked polyurethane network” case.

Angle	ϑ_0 (°)	K_{angle} (kJ mol ⁻¹ rad ⁻²)
PEG		
COH-COC-COC	121.43	35.5
COC-COC-COC	114.2	38.1
Triisocyanate Crosslinker		
OCO-CC-CC	119.73	241.6
CC-CC-CC	147.5	474.8
CC-NCO-NCC	120.73	550.6
NCO-NCC-OCN	74	122
NCO-NCC-CC	136.12	197.8
CC-CC-NCC	163.9	153

Table S7. Angle type parameters for the “PAMAM dendrimer” case.

Angle	ϑ_0 (°)	K_{angle} (kJ mol ⁻¹ rad ⁻²)
dendrimer		
NCCC-CC-CO	149.0	370
CC-CO-1NC	96.0	480
CO-1NC-NC	128.0	160
CO-1NC-1NC	126.0	200
1NC-1NC-CC	138.0	30
1NC-CC-COOC	157.0	150
CO-1NC-2NC	120.0	180
1NC-2NC-CC	119.0	50
2NC-CC-COOC	152.0	87
CC-2NC-CC	78.0	100

Table S8. Angle type parameters for “hyperbranched polymer” case.

Angle	ϑ_0 (°)	K_{angle} (kJ mol ⁻¹ rad ⁻²)
3, 5-dihydroxybenzoic acid		
CCR-CCR-COH	142.8	3071
CCR-CCR-COOH	75.2	3410
COH-CCR-CCR	83.5	2476
COH-CCR-CCR	142.8	5396
CCR-CCR-COOH	134.8	4022
COH-CCR-CCR	83.8	1853
1, 6-dibromohexane		
CCB-CCA-CCB	158.3	150.5

Table S9. Dihedral type parameters for the "PAMAM dendrimer" case.

Dihedral	ϑ_0 (°)	K_{dihedral} (kJ mol ⁻¹)	multiplicity
dendrimer			
NCCC-CC-CO-1NC	0	10	1
CC-CO-1NC-NC	0	8	2
CO-1NC-1NC-CC	0	8	1
CO-1NC-2NC-CC	0	7	1
1NC-2NC-CC-COOC	0	3	2
CC-2NC-CC-COOC	0	5	1
CC-CO-1NC-1NC	0	7	2
CC-CO-1NC-2NC	0	8	2

S3- Details of MD simulations

The simulation box for various cases was built and the relaxation steps were done with the following settings on GROMACS 2020.

Homo-polymerization of lactic acid (test case 1)

25,000 monomers of PLA were randomly placed in a simulation box. An energy minimization step using a steep integrator was performed on the simulation box, followed by a 50 ns equilibration under *NPT* conditions at 298 K and 1 bar pressure with a 20 fs time-step. The v-rescale thermostat and Parrinello-Rahman barostat were used for controlling the temperature and pressure during the equilibration. Thereafter the reactions were switched on and the polymerization was done.

Crosslinked polyurethane network (test case 2)

For crosslinking the monomers, 999 molecules of polyethylene glycol (PEG) and 666 molecules of triisocyanate crosslinker were randomly inserted into the simulation box. For dangling chain containing cases, 10 % of PEG hydroxyl groups were replaced by polyethylene glycol monomethyl ether (mPEG). Following energy minimization by the steep integrator, the system was equilibrated under constant *NPT* conditions at 300 K and 1 bar pressure with a 20 fs time-step during 10 ns. The Berendsen thermostat in the velocity rescaling scheme and Berendsen barostat were used for the *NPT* conditions. Thereafter the reaction between the hydroxyl and isocyanate bead was done.

PAMAM dendrimer (test case 3)

The construction of the dendrimer was performed step-by-step. First, 10 molecules of 0.5th generation were placed in a simulation box containing 12000 ethylenediamine (EDA) molecules solvated in methanol. Thereafter an energy minimization by using a steep integrator and 50 ns of relaxation under *NPT* conditions at 300 K and 1 bar pressure with a 10 fs time-step was performed using the v-rescale thermostat and Parrinello-Rahman barostat. After these steps, the reactions were switched on and the 1st generation of dendritic molecules was constructed. After removing unreacted species from the simulation box, 12000 methyl acrylate (MA) molecules were added to the box to perform the next step of the

reaction. The same relaxation as for the previous step was done followed by the reaction steps which produces the 1.5th generation structures. These steps were iterated to produce 7th generation structures of PAMAM dendrimers.

Hyperbranched polymer (test case 4)

First of all, 2500 molecules of 1,6-dibromohexane, 2500 molecules of 3,5-dihydroxybenzoic acid and 5000 molecules of dimethylformamide (DMF) were inserted into the simulation box. Following energy minimization by using a steep integrator, the system was equilibrated under *NPT* conditions at 298 K and 1 bar pressure with a 5 fs time-step during 5 ns. The *v*-rescale thermostat and Berendsen barostat were used for the *NPT* conditions.

S4- Crosslinked polyurethane networks

Figure S4 shows the connectivity graphs of test case 2 (Crosslinked polyurethane networks).

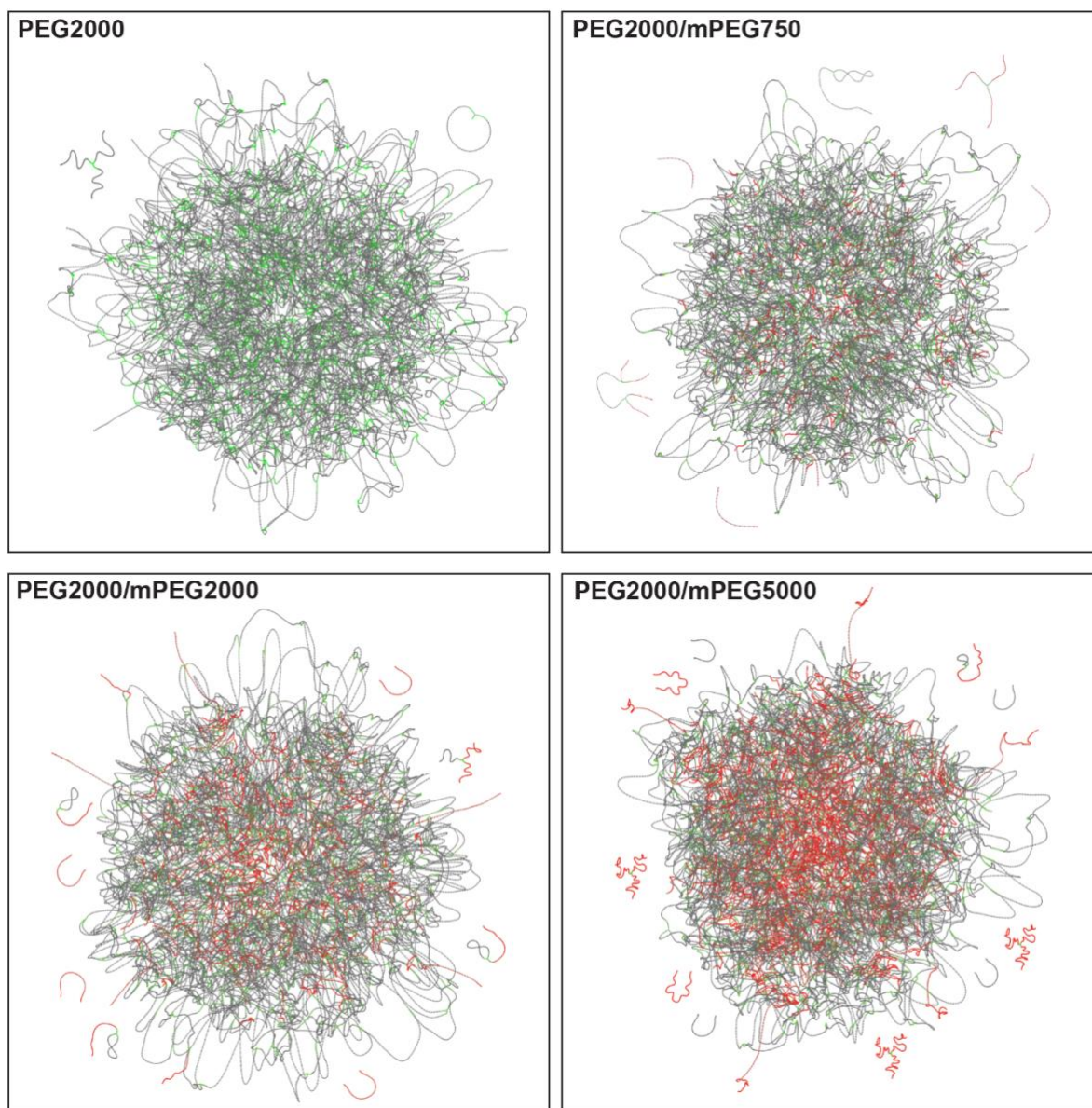


Figure S4. Molecular structure of Final Networks for cross-linked polyurethane case.

S5- Hyperbranched polymers

Determining the reactivity of the hydroxyl groups through the analysis of reaction products of 1, 6-dibromohexane and 3,5-dihydroxybenzoic acid by ^1H NMR and GPC analysis is difficult. For this reason, the reference paper designed a model reaction of monofunctional 1-bromohexane with 3,5-dihydroxybenzoic acid under the same reaction conditions. The products of this reaction were determined by ^1H NMR spectrum (See Figure S5). We mimicked this reaction in simulation too. The reaction probabilities of CCB with COOH , COH_A , and COH_B beads were set to 1, 0.2, and 0.3, respectively. Table S10 lists the product ratios obtained by ^1H NMR analysis and MD simulation.

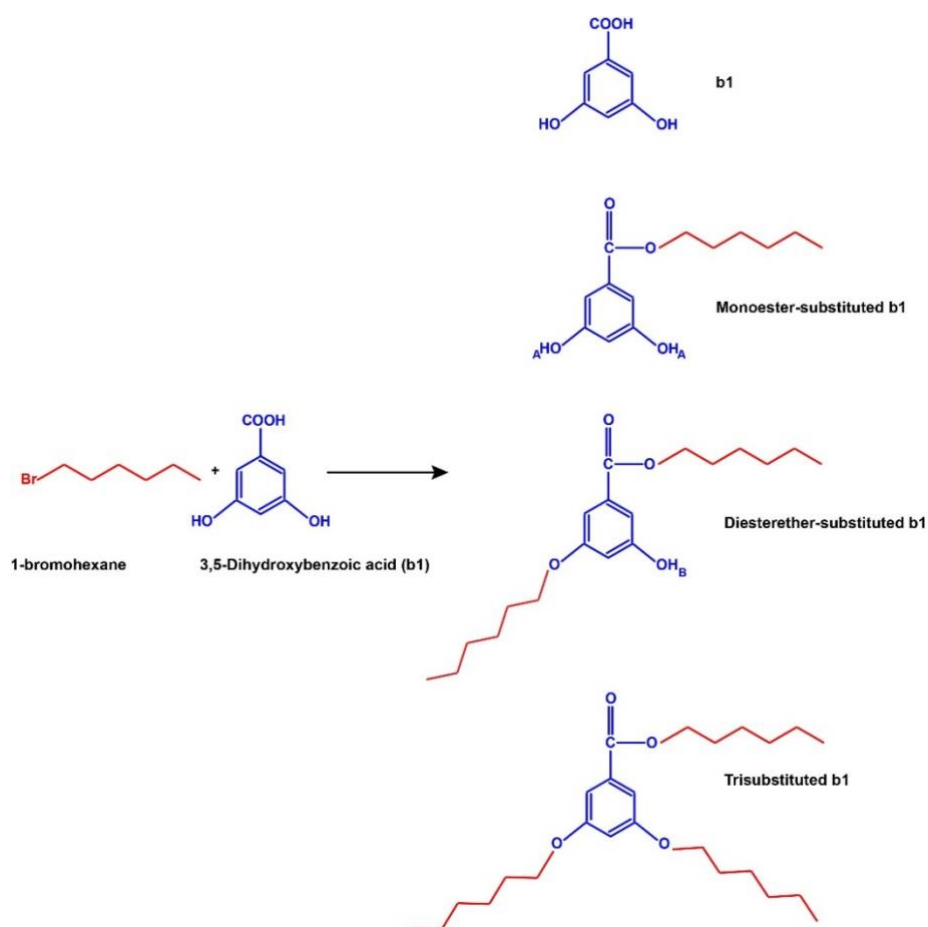


Figure S5. The reaction scheme of 1-bromohexane and 3,5-dihydroxybenzoic acid.

Table S10. The percentage of unreacted, monoester-substituted, diesterether-substituted and trisubstituted b1 in products from 1-bromohexane and 3,5-dihydroxybenzoic acid (1:1 molar ratio).

	b1	Monoester-substituted b1	Diesterether-substituted b1	Trisubstituted b1
Percentage of products (^1H NMR)	23.0 %	57.8 %	16.0 %	3.2 %
Percentage of products (simulation)	23.8 %	56.6 %	15.4 %	4.2 %