Supporting information for: UV-curable Biobased Polyacrylates based on a Multifunctional Monomer derived from Furfural

Jules Stouten\textsuperscript{a}, Danny E. P. Vanpoucke\textsuperscript{a,b}, Guy Van Assche\textsuperscript{c}, Katrien V. Bernaerts\textsuperscript{a,*}

\textsuperscript{a} Aachen-Maastricht Institute for Biobased Materials (AMIBM), Faculty of Science and Engineering, Maastricht University, Brightlands Chemelot campus, Urmonderbaan 22, 6167 RD Geleen, The Netherlands.

\textsuperscript{b} Institute for Materials Research (IMO), Hasselt University, 3590 Diepenbeek, Belgium.

\textsuperscript{c} Department of Physical Chemistry and Polymer Science, Faculty of Engineering Sciences, Vrije Universiteit Brussel (VUB), Pleinlaan 2, 1050 Brussels, Belgium.

* To whom correspondence should be addressed.

E-mail: katrien.bernaerts@maastrichtuniversity.nl Telephone: +31 433882636

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1. Structural stability and vibrational spectrum

The molecular structure of the monomer (1) and the four conformers of the (1)-dimer are optimized using a conjugate gradient algorithm with an energy-based convergence criterion. To validate the (local) ground state nature of the conformers, the vibrational spectrum is determined using the finite difference approach as implemented in the VASP code.¹ Direct diagonalization of the obtained Hessian matrix of the dimers resp. monomer resulted in three vibrational modes with zero amplitude (corresponding to translations), and five resp. four imaginary modes corresponding to three molecular rotations and two resp. one modes corresponding to the rotation of the methyl groups.²-³ Investigation of the potential energy surface (PES) of the methyl rotation of the monomer (cf., Figure S2), however, shows the optimized structure (rotation of 0°) to be the ground state. This indicates there is a mixing of the vibrational modes, making it necessary to project out both translational and rotational modes of the molecules.
1.1 Projecting out the translational and rotational modes of the hessian matrix

We start from the mass-weighted Hessian matrix in Cartesian coordinates

$$H_{i,j,\alpha,\beta}^{C} = \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 V}{\partial x_{i,\alpha} \partial x_{j,\beta}},$$

with $V$ the potential of the system, $m_i$ the mass of atom $i$, and $x_{i,\alpha}$ the displacement in Cartesian coordinates of atom $i$ along the direction $\alpha$ ($\alpha \in x, y, z$). Projecting out the rotational and translational modes (or transforming to internal coordinates) is done through a unitary transformation. The unitary transformation matrix consists of six columns representing the modes to project out, and an additional $3N-6$ orthonormal vectors creating a full orthonormal basis.

**Figure S1.** Potential energy surface of methyl rotation on model compound (1).
Before we construct this unitary matrix, the centre of mass of the system is shifted to the origin. Since the systems coordinates are provided under periodic boundary conditions, we adapt the scheme suggested by Bai and Breen.

For each of the three Cartesian directions the centre of mass component is calculated independently as follows. Assume \( \alpha_i \in [0,1[ \) to be the direct coordinate of atom \( i \) along the \( \alpha \) direction, and \( l_\alpha \) the distance between periodic copies along this direction. The atomic coordinates \( \alpha_i \) are projected onto a unit-circle using the transformation

\[
\begin{align*}
\theta_i &= \alpha_i 2\pi \\
x_i &= \cos(\theta_i) \\
y_i &= \sin(\theta_i)
\end{align*}
\]

The respective centre of mass component in the plane of the circle is obtained via

\[
\begin{align*}
\bar{x} &= \frac{\sum_\iota m_i x_i \iota}{\sum_\iota m_i} \\
\bar{y} &= \frac{\sum_\iota m_i y_i \iota}{\sum_\iota m_i}
\end{align*}
\]

and can be transformed back to the centre of mass component in Cartesian space via

\[
\bar{\alpha} = l_\alpha \frac{\bar{\theta}}{2\pi} = l_\alpha \frac{\text{atan}2(-\bar{y}, -\bar{x})}{2\pi} + \pi.
\]

This approach only breaks down if the centre of mass component in the plane of the circle is located at the origin, which would indicate a uniform distribution of the atoms along this specific (infinite) periodic direction. In this degenerate case, any point along this direction would be a valid centre of mass, so the Cartesian component is defaulted to zero.
With the system shifted to the centre of mass, the columns of the unitary matrix corresponding to the translations are given by an (infinitesimal) unit translation of the system along each of the three Cartesian directions. This is done using mass-weighted coordinates \( q_{i,\alpha} = \sqrt{m_i} x_{i,\alpha} \).

\[
\begin{align*}
U_1 &= \left( \sqrt{m_1}, 0, 0, \sqrt{m_2}, 0, 0, \ldots \right)^T, \\
U_2 &= \left( 0, \sqrt{m_1}, 0, 0, \sqrt{m_2}, 0, \ldots \right)^T, \\
U_3 &= \left( 0, 0, \sqrt{m_1}, 0, 0, \sqrt{m_2}, \ldots \right)^T.
\end{align*}
\]

The three columns corresponding to the rotations on the other hand represent (infinitesimally) small rotations around the three principal axes of rotation of the system. The principal axes of rotation are calculated as the eigenvectors \( v_{i,\alpha} \) of the moment of inertia tensor:

\[
I = \begin{pmatrix}
\sum_i \left( q_{i,y}^2 + q_{i,x}^2 \right) & -\sum_i q_{i,x} q_{i,y} & -\sum_i q_{i,x} q_{i,z} \\
-\sum_i q_{i,y} q_{i,x} & \sum_i \left( q_{i,x}^2 + q_{i,z}^2 \right) & -\sum_i q_{i,y} q_{i,z} \\
-\sum_i q_{i,z} q_{i,x} & -\sum_i q_{i,z} q_{i,y} & \sum_i \left( q_{i,x}^2 + q_{i,y}^2 \right)
\end{pmatrix}.
\]

An infinitesimal rotation of atom \( i \) around the principal axis \( v_{i,\alpha} \) will then be oriented along the tangent of the circle performed by the position vector \( q_i \): \( R_{i,\alpha} = q_i \times v_{i,\alpha} \).

This allows us to write the three columns corresponding to the rotational modes as:

\[
\begin{align*}
U_4 &= \left( R_{1,x}, R_{2,x}, \ldots \right)^T, \\
U_5 &= \left( R_{1,y}, R_{2,y}, \ldots \right)^T, \\
U_6 &= \left( R_{1,z}, R_{2,z}, \ldots \right)^T.
\end{align*}
\]

In this, \( R_{1,x} \) is the 3-component vector representing the rotation of atom 1 around the \( x \) principal axis.
Using a modified Gram-Schmidt orthogonalisation scheme the remaining 3N-6 columns of the unitary transformation matrix are constructed. The Hessian matrix is transformed to internal coordinates and the translational and rotational modes are projected out:

\[ H^{\text{int}} = U^\dagger H^C U \]

Applying this approach to the hessian matrices of the monomer and dimers shows all structures to be in a local minimum with no imaginary modes remaining. As a result, these clean vibrational spectra can be used to calculate the vibrational energy contributions to the Gibbs free energy.

1.2 Gibbs free energy

![Figure S2. Gibbs free energy of formation of the four different conformers.](image-url)
2. Density functional theory calculated chemical shifts

2.1 Absolute versus relative positions

The chemical shift of an atom strongly depends on its chemical environment, as well as the bond length with its neighbours. Practical quantum mechanical calculations use approximate functionals in the description of the exchange and correlation functions. Furthermore, these calculations are performed assuming zero temperature and pressure. As a result, small deviations in the bond lengths compared to the experimental reality are to be expected. To investigate the influence of such changes in the bond lengths, we calculated the chemical shifts of the HHc conformer, in which all the bond lengths are stretched by ±1 and ±2%.
Figure S3. Change in the chemical shift due to a stretching/compressing of all chemical bonds.

As can be seen in the above figure, the chemical shift changes almost linearly (numerical values are available in accompanying excel sheet, part of the SI) and quite significantly: 3 to 4.5 ppm per % change in bond length for the carbon atoms, and 0.3 to 0.4 ppm per % change in bond length for the hydrogen atoms. Although there is a wide spread in these values, this spread is not arbitrary. Comparison to the full NMR spectrum indicates that the atoms belonging to the same distinct band show a very similar change in chemical shift. In contrast, there is no clear relation between the absolute peak position and the expected change in chemical shift.

This observation has some important consequences. Firstly, it shows that a mismatch between the simulated and experimental spectrum cannot be resolved by a single unique shift of the simulated
spectrum. Secondly, a scaling of the spectral range cannot resolve such a mismatch either. However, using the obtained knowledge that sub-groups exist in the spectrum, it is possible to obtain a more closely related qualitative comparison with experiment by using a different shift for each sub-group. This is implemented in our HIVE toolbox. We have selected the best fit shift for each of the groups defined in the manuscript based on the comparison of the HHe conformer spectrum and the experimental spectrum, and applied these same shifts to the subgroups of all 4 conformers. The resulting (shifted) spectra are shown in Figure S4 and S5. The shifts used for the different subgroups are shown in Table S1.

**Table S1.** Sub-group shifts for comparison of calculated and experimental NMR spectra.

| Sub-group shifts used for H (ppm) |          |
|----------------------------------|----------|
| H_{br}                           | 30.793   |
| H_{CB} + H_{2}                   | 30.961   |
| H_{3}                            | 30.978   |

| Sub-group shifts used for C (ppm) |          |
|----------------------------------|----------|
| C_{O2} + C_{H-O}                 | 168.138  |
| C_{O2}                           | 172.093  |
| C_{CB} + C_{H2}                  | 175.366  |
| C_{H3}                           | 181.467  |
Figure S4. Comparison of calculated and experimental chemical shifts for hydrogen. The dotted lines indicate experimental positions. Calculated spectra have a Gaussian shape with a 0.01 ppm variance.
Figure S5. Comparison of calculated and experimental chemical shifts for carbon. The dotted lines indicate experimental positions. Calculated spectra have a Gaussian shape with a 0.1 ppm variance.
2.2 NMR of Oxygen

**Figure S6.** Ball-and-stick representation of a HHc dimer of (1). The atomic sites giving rise to the simulated oxygen NMR spectrum are indicated.

**Table S2.** Calculated chemical shift $\delta$ (ppm), sorted smallest to largest. The atomic site indicated, as defined in Figure S6, with A and B used to distinguish between the monomers making up the dimer.

| Chemical shift O | HHc $\delta$ site | HTc $\delta$ site | HHb $\delta$ site | HTb $\delta$ site |
|------------------|-------------------|-------------------|-------------------|-------------------|
| HHc              |                   |                   |                   |                   |
| -110.21 O$_{br}$ B | -114.20 O$_{br}$ B | -103.68 O$_{br}$ A | -107.34 O$_{br}$ A |
| -108.57 O$_{br}$ A | -106.14 O$_{br}$ A | -99.95 O$_{br}$ B | -107.09 O$_{br}$ B |
| 71.11 O$_{ace}$ A | 65.22 O$_{ace}$ B | 76.70 O$_{ace}$ A | 68.31 O$_{ace}$ A |
| 73.55 O$_{ace}$ B | 70.33 O$_{ace}$ A | 95.76 O$_{ace}$ B | 68.40 O$_{ace}$ B |
| 283.15 O$_{r}$ A | 278.97 O$_{r}$ A | 295.20 O$_{r}$ B | 300.10 O$_{r}$ B |
| 283.24 O$_{r}$ B | 288.62 O$_{r}$ B | 303.67 O$_{r}$ A | 300.30 O$_{r}$ A |
3. Experimental spectra

Figure S7. (a) $^1$H-NMR and (b) $^{13}$C-NMR spectra of 4HCP.
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**Figure S12.** DEPT-90 of poly(4CPA).

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Figure S14. DSC traces of copolymers poly(4CPA-co-IBA) (P1), poly(4CPA-co-MA) (P2) and poly(4CPA-co-LA) (P3).

Figure S15. MS spectrum of model dimer.
Figure S16. DEPT-135 of the dimers of (1).

DEPT-135 (CH$_2$ = negative, CH and CH$_3$ = positive)
Figure S17. HSQC of the dimers of (1).
**Figure S18.** Swell ratio in CHCl₃ of the prepared crosslinked films of poly(4CPA-co-LA) P3-3/7 containing various contents of acetophenone, and poly(4CPA-co-MA) P2-3/7 containing 1 wt% acetophenone.

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