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## Directed dihydroxylation of a poly(cyclooctadienol) toward densely-hydroxylated polyol adhesives†

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Adhesives play an important role in an array of industries, including construction, medicine, paper products, and more. Specialty applications are expanding and evolving to require more niche adhesives to suit unique needs. In one of its many applications, poly(vinyl alcohol) (PVA) serves as a water-soluble adhesive; yet, PVA's adhesive ability is ultimately constrained by its fixed degree of hydroxylation and head-to-tail construction. In this work, we synthesize a water-soluble polyol that features a higher density of hydroxylation than PVA and exhibits thermal and adhesive properties comparable to PVA and Elmer's® clear glue. We do so *via* catalytic dihydroxylation of a polybutadiene derivative formed *via* ring-opening metathesis polymerization of a cyclooctadiene with a single allylic alcohol. Notably, such global catalytic dihydroxylation relies on allylic and homoallylic hydroxyl moieties as directing groups, and as such, could not previously be implemented in the context of unfunctionalized polybutadiene. Hence, this work provides an alternative entry to polyols with high alcohol group content toward water-soluble specialty adhesives.

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From aircraft to masking tape, polymer-based adhesives are indispensable in a variety of modern technologies.<sup>1</sup> The demand for new specialty adhesives is ever-increasing, with a need for desirable properties that align with future applications, such as sustainable glues or adherents in electric vehicles.<sup>2,3</sup> Polyvinyl alcohol (PVA) is one such industrial adhesive utilized in manufacturing, packaging, medicine, and numerous other applications.<sup>4</sup> PVA is synthesized from the hydrolysis of polyvinyl acetate (PVAc), derived from the atactic head-to-tail addition of vinyl acetate monomers<sup>5</sup> *via* free radical polymerization. The 1,3-alcohol structure is maintained consistently throughout the hydrolyzed polymer.<sup>6</sup> To understand the effect of polyol structure on adhesion, we developed a densely-functionalized polyol **P2**, and compared its thermal and adhesive properties to PVA and Elmer's® clear glue. Our goal of synthesizing **P2** motivated the development of a new method for generating polymeric 1,2-diols *via* directed dihydroxylation of an unsaturated polymer.

To access such densely hydroxylated polyols, a different synthetic strategy would be required compared to the one utilized to make PVA. In particular, direct dihydroxylation of a formal polybutadiene derivative prepared *via* ring-opening metathesis polymerization (ROMP) of cyclooctadienol **M1** (Fig. 1)

appeared to be a promising route. Indeed, Upjohn dihydroxylation using catalytic osmium tetroxide<sup>7</sup> had been demonstrated in the context of poly(oxa-norbornene)s and poly(norbornene)s prepared *via* ROMP;<sup>8–12</sup> however, this approach has previously failed in the context of polybutadiene<sup>13,14</sup> and is almost non-existent in poly(cyclooctadiene) derivatives, save for a reference in one thesis.<sup>15</sup> The key challenges encountered in the dihydroxylation of polybutadiene are phase separation and poor polymer solubility. We hypothesized that pre-installed (homo-)allylic hydroxyl groups would both improve the polymer solubility in the polar reaction media common to Upjohn dihydroxylation and serve as directing groups that could accelerate reactivity. Reports of allylic alcohols undergoing osmium-catalyzed dihydroxylation support the directing ability of hydroxyl groups, resulting in highly-hydroxylated compounds.<sup>16</sup> Thus, we imagined an analogous reactivity profile to previous reports,<sup>17</sup> where directed dihydroxylation could be applied to unsaturated polymers by incorporating (homo-)allylic alcohols.

Synthesis of the densely-hydroxylated polyol **P2** was successfully carried out in three steps (Fig. 2A). First, **M1** was pro-



Fig. 1 Retrosynthetic analysis applied to polyol **P2**.

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**Fig. 2** (A). Reaction scheme and photographs for synthesis of **P2**. Representative  $^1\text{H}$  NMR spectra (B), TGA (C), and DSC plots (D) for **P1** ( $10\text{ }^\circ\text{C min}^{-1}$ ;  $M_n = 86.7\text{ kg mol}^{-1}$ ) and **P2** ( $20\text{ }^\circ\text{C min}^{-1}$ ). \*Equivalents calculated and reported relative to **P1** repeat unit.

duced *via* Riley oxidation<sup>18,19</sup> of 1,5-cyclooctadiene (COD). Next, a version of the 3<sup>rd</sup>-generation Grubbs catalyst<sup>20–22</sup> was employed for the ROMP of **M1** to form the partially-hydroxylated unsaturated polymer **P1** as a brown rubbery solid (Fig. 2A). Notably, in the  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum of **P1**, we observe two distinct methine resonances at 4.07 ppm and 4.41 ppm with nearly equal integration (Fig. 2B), which suggests random head-to-head and head-to-tail linking of successive monomers and/or ring-opening at both alkenes of **M1**. Complete dihydroxylation (>95%) of **P1** was confirmed using  $^1\text{H}$  NMR analysis which revealed the total disappearance of alkene resonances (Fig. 2B). Gel permeation chromatography with multi-angle light scattering (GPC-MALS) with THF as the eluent was utilized to determine the number-average molecular weight ( $M_n$ ) and dispersity ( $D$ ) of different batches of **P1** produced by varying the monomer-to-initiator ratio (Fig. S1 and S2<sup>†</sup>):  $M_n = 86.7\text{ kg mol}^{-1}$  and  $D = 2.37$  for one batch, and  $M_n = 163\text{ kg mol}^{-1}$  and  $D = 2.41$  for another. Additionally, molecular weight control was achievable by incorporating simple *cis*-alkenes as chain transfer agents,<sup>23,24</sup> reducing metathesis catalyst loading (Table S1<sup>†</sup>). Lastly, OsO<sub>4</sub>-catalyzed dihydroxylation of both batches of **P1** was performed to afford polyol **P2** in good yield (82%) as a white material with a cotton-like appearance (Fig. 2A). Residual osmium content is estimated to be  $8.6\text{ }\mu\text{g mg}^{-1}$  for one batch of **P2**, and  $1.3\text{ }\mu\text{g mg}^{-1}$  for another using inductively coupled plasma mass spectrometry (ICP-MS), corresponding to an 82% and 97% removal of osmium from the material post-workup. For the remainder of the manuscript we focus on **P2** derived from the first batch of **P1** ( $M_n = 86.7\text{ kg mol}^{-1}$ ), as this molecular weight value more closely reflects the PVA control ( $89\text{--}98\text{ kg mol}^{-1}$ ).

With **P1** and **P2** in hand, we performed thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of these materials to evaluate their thermal properties. **P1**

( $86.7\text{ kg mol}^{-1}$ ) had a temperature of decomposition at 5% weight loss ( $T_{d, 5\%}$ ) of  $260\text{ }^\circ\text{C}$  and  $T_{d, 10\%}$  of  $330\text{ }^\circ\text{C}$  at 10% weight loss, while the corresponding **P2** had a  $T_{d, 5\%}$  of  $191\text{ }^\circ\text{C}$  and  $T_{d, 10\%}$  of  $234\text{ }^\circ\text{C}$  (Fig. 2C). Notably, **P2** retained a significant amount of charred material and exhibited a total weight loss of about 54%, even when heated to  $550\text{ }^\circ\text{C}$ . The glass transition temperature ( $T_g$ ) of **P1** is  $8\text{ }^\circ\text{C}$ , while the  $T_g$  of **P2** is considerably higher at  $101\text{ }^\circ\text{C}$  (Fig. 2D). This dramatic difference in  $T_g$  is expected: more thermal energy is required to impart chain mobility with increased inter- and intra-chain hydrogen bonding.<sup>25</sup> Notably, the  $T_g$  of **P2** is even higher than that of PVA (reported in the  $75\text{--}85\text{ }^\circ\text{C}$  range);<sup>26</sup> yet, in further contrast with PVA,<sup>27</sup> **P2** exhibits no melting behavior *via* DSC, suggesting amorphous morphology, although this feature may be absent because of lower-temperature degradation: **P2** undergoes degradation ( $T_{d, 5\%} = 191\text{ }^\circ\text{C}$ ) before PVA's reported melting temperature ( $>220\text{ }^\circ\text{C}$ ).<sup>28</sup>

Having established the effects of dense backbone hydroxylation on thermal properties, we sought to explore its effects on adhesion using the lap shear test. As our controls, we tested a similar batch of **P1** ( $92.2\text{ kg mol}^{-1}$ , Fig. S3<sup>†</sup>), poly(ethylene glycol) (PEG) ( $20\text{ kg mol}^{-1}$ ), PVA ( $89\text{--}98\text{ kg mol}^{-1}$ ), and commercial Elmer's® clear glue (an aqueous emulsion of PVAc, PVA, and propylene glycol).<sup>29</sup> As our substrate, we selected glass slides, because their hydrophilic surfaces are wetted well by the aqueous solutions of the polar polymers. The adhered samples were prepared by applying approximately the same amount of adhesive by weight in solution to a surface area of  $635\text{ mm}^2$  (1 in by 1 in) and clamping the two surfaces together using binder clips (Fig. 3A). After allowing the samples to dry for several days, they were further annealed in a vacuum oven around each adhesive's  $T_g$  for 3 hours to minimize macroscopic inhomogeneity in the adhesive film between the glass substrates.

Lap shear tests were performed by clamping both ends of the adhered substrates (Fig. 3A) and pulling at a constant





**Fig. 3** (A). Illustration of a typical sample for analysis. (B). Plot of force (N) versus displacement (mm) for a representative sample closest to the average for the adhesive.

strain rate ( $0.05 \text{ mm s}^{-1}$ ) in opposing directions. Approximately 10 replicates were tested for each sample, and the representative results are plotted in Fig. 3B and summarized in Table 1. Good agreement was observed among the **P2**, **P1**, PVA, and Elmer's® clear glue replicates before the yield point (Fig. S4–S7†), while PEG exhibited a broader distribution of yield strength values (Fig. S8†).

The yield strength measured for **P2** ( $0.17 \pm 0.02 \text{ MPa}$ ) proved to be comparable to PVA ( $0.16 \pm 0.01 \text{ MPa}$ ) and Elmer's® clear glue ( $0.18 \pm 0.01 \text{ MPa}$ ). Additionally, **P2** outperforms PEG ( $0.10 \pm 0.04 \text{ MPa}$ ) in yield consistency and failure mode—PEG is brittle, while **P2** exhibits more plastic behavior. **P1** demonstrated poor adhesive performance ( $0.0750 \pm 0.002 \text{ MPa}$ ), displaying creep-like behavior when pulled, evident both visually and in a steady decline in measured force over greater displacements (Fig. S4†). These results indicate that **P2** performs similarly to PVA and Elmer's® clear glue; additionally, increasing degree of hydroxylation from **P1** to **P2** corresponds to an over two-fold increase in adhesive strength.

Spanning a variety of industries, adhesives play a critical role in our modern world. PVA is one such polyol adhesive

with commercial significance, and we hypothesized that tuning polymer structure and hydroxyl group density would directly impact adhesive and thermal properties. In conclusion, we developed a highly-hydroxylated polyol **P2** that could serve as an adhesive for specialty applications where moderate strength, water-solubility, and thermal stability are desirable. **P2** performed well when compared to its adhesive counterparts and significantly outperformed its less decorated precursor **P1**. Based on literature precedents, we installed (homo-)allylic hydroxyl directing groups to impart both improved solubility to the polymer and to accelerate dihydroxylation which had previously not been observed with hydroxyl-free polybutadiene.

## Author contributions

The idea for this work was conceived by A.V.Z. All experiments and analysis were performed by L.S.C., and A.V.Z. supervised this work. This manuscript was written and revised through contributions of both authors, with approval given to the final version of this document.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Conflicts of interest

There are no conflicts to declare.

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**Table 1** Average adhesive data from lap shear tests. Yield strength values were calculated by dividing the yield force (N) by the adhered area of the samples ( $635 \text{ mm}^2$ )

Adhesive	Yield strength (MPa)
PEG	$0.10 \pm 0.04$
PVA	$0.16 \pm 0.01$
Elmer's	$0.18 \pm 0.01$
<b>P1</b>	$0.0750 \pm 0.002$
<b>P2</b>	$0.17 \pm 0.02$



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## References

- I. Skeist, *Handbook of Adhesives*, Springer, New York, NY, United States, 1989.
- C. R. Matos-Pérez, J. D. White and J. J. Wilker, Polymer Composition and Substrate Influences on the Adhesive Bonding of a Biomimetic, Cross-Linking Polymer, *J. Am. Chem. Soc.*, 2012, **134**(22), 9498–9505, DOI: [10.1021/ja303369p](https://doi.org/10.1021/ja303369p).
- 3M Continues History of Innovating for The Future|Adhesives & Sealants Industry. <https://www.adhesivesmag.com/articles/101144-3m-continues-history-of-innovating-for-the-future> (accessed 2024-12-02).
- T. S. Gaaz, A. B. Sulong, M. N. Akhtar, A. A. H. Kadhum, A. B. Mohamad and A. A. Al-Amiery, Properties and Applications of Polyvinyl Alcohol, Halloysite Nanotubes and Their Nanocomposites, *Molecules*, 2015, **20**(12), 22833–22847, DOI: [10.3390/molecules201219884](https://doi.org/10.3390/molecules201219884).
- C. S. Marvel and C. E. Denoon Jr., The Structure of Vinyl Polymers. II.1 Polyvinyl Alcohol, *J. Am. Chem. Soc.*, 1938, **60**(5), 1045–1051, DOI: [10.1021/ja01272a018](https://doi.org/10.1021/ja01272a018).
- M. L. Hallensleben, Polyvinyl Compounds, Others, in *Ullmann's Encyclopedia of Industrial Chemistry*, John Wiley & Sons, Ltd, 2000. DOI: [10.1002/14356007.a21\\_743](https://doi.org/10.1002/14356007.a21_743).
- V. VanRheenen, R. C. Kelly and D. Y. Cha, An Improved Catalytic OsO<sub>4</sub> Oxidation of Olefins to cis-1,2-Glycols Using Tertiary Amine Oxides as the Oxidant, *Tetrahedron Lett.*, 1976, **17**(23), 1973–1976, DOI: [10.1016/S0040-4039\(00\)78093-2](https://doi.org/10.1016/S0040-4039(00)78093-2).
- S. Meier, H. Reisinger, R. Haag, S. Mecking, R. Mülhaupt and F. Stelzer, Carbohydrate Analogue Polymers by Ring Opening Metathesis Polymerisation (ROMP) and Subsequent Catalytic Dihydroxylation, *Chem. Commun.*, 2001, **9**, 855–856, DOI: [10.1039/B100680K](https://doi.org/10.1039/B100680K).
- N. Li, X. Qu, L. Wang, Q. Tian, Y. Chen, X. Yao, S. Chen and S. Jin, Chemical Synthesis of Chitosan-Mimetic Polymers via Ring-Opening Metathesis Polymerization and Their Applications in Cu<sup>2+</sup> Adsorption and Catalytic Decomposition, *Polym. Chem.*, 2020, **11**(41), 6688–6700, DOI: [10.1039/D0PY00668H](https://doi.org/10.1039/D0PY00668H).
- M. Wathier, S. S. Stoddart, M. J. Sheehy and M. W. Grinstaff, Acidic Polysaccharide Mimics via Ring-Opening Metathesis Polymerization, *J. Am. Chem. Soc.*, 2010, **132**(45), 15887–15889, DOI: [10.1021/ja106488h](https://doi.org/10.1021/ja106488h).
- I. K. Tennie and A. F. M. Kilbinger, Polymeric <sup>19</sup>F MRI Contrast Agents Prepared by Ring-Opening Metathesis Polymerization/Dihydroxylation, *Macromolecules*, 2020, **53**(23), 10386–10396, DOI: [10.1021/acs.macromol.0c01585](https://doi.org/10.1021/acs.macromol.0c01585).
- N.-T. Lin, S.-L. Lee, J.-Y. Yu, C. Chen, S.-L. Huang and T.-Y. Luh, Poly(Bisnorbornanediol), *Macromolecules*, 2009, **42**(18), 6986–6991, DOI: [10.1021/ma901302e](https://doi.org/10.1021/ma901302e).
- M. Nicol, *Modification of Polydienes via Homogenous Catalysis*, Thesis, University of St Andrews, 1998. <https://research-repository.st-andrews.ac.uk/handle/10023/15183> (accessed 2024-08-21).
- P. Lamprecht, *Chemische Modifizierung von Synthetikgummi durch polymeranaloge Reaktionen*, Doctoral dissertation, Staats- und Universitätsbibliothek Hamburg Carl von Ossietzky, 2012. <https://ediss.sub.uni-hamburg.de/handle/ediss/4455> (accessed 2024-08-21).
- S. S. Stoddart, *Surface Grafting of Synthetic Hydrophilic Polymers via Ring Opening Metathesis Polymerization for Biomedical Applications*, 2005.
- H. C. Kolb, M. S. VanNieuwenhze and K. B. Sharpless, Catalytic Asymmetric Dihydroxylation, *Chem. Rev.*, 1994, **94**(8), 2483–2547, DOI: [10.1021/cr00032a009](https://doi.org/10.1021/cr00032a009).
- Hydrogen-bonding-mediated directed osmium dihydroxylation. <https://chem.web.ox.ac.uk/publication/359724/scopus> (accessed 2024-11-20).
- J. Młochowski and H. Wójtowicz-Młochowska, Developments in Synthetic Application of Selenium(IV) Oxide and Organoselenium Compounds as Oxygen Donors and Oxygen-Transfer Agents, *Molecules*, 2015, **20**(6), 10205–10243, DOI: [10.3390/molecules200610205](https://doi.org/10.3390/molecules200610205).
- H. L. Riley, J. F. Morley and N. A. C. Friend, 255. Selenium Dioxide, a New Oxidising Agent. Part I. Its Reaction with Aldehydes and Ketones, *J. Chem. Soc. (Resumed)*, 1932, 1875–1883, DOI: [10.1039/JR9320001875](https://doi.org/10.1039/JR9320001875).
- J. A. Love, J. P. Morgan, T. M. Trnka and R. H. Grubbs, A Practical and Highly Active Ruthenium-Based Catalyst That Effects the Cross Metathesis of Acrylonitrile, *Angew. Chem., Int. Ed.*, 2002, **41**(21), 4035–4037, DOI: [10.1002/1522-3773\(20021104\)41:21<4035::AID-ANIE4035>3.0.CO;2-I](https://doi.org/10.1002/1522-3773(20021104)41:21<4035::AID-ANIE4035>3.0.CO;2-I).
- K. D. Camm, N. Martinez Castro, Y. Liu, P. Czechura, J. L. Snelgrove and D. E. Fogg, Tandem ROMP-Hydrogenation with a Third-Generation Grubbs Catalyst, *J. Am. Chem. Soc.*, 2007, **129**(14), 4168–4169, DOI: [10.1021/ja071047o](https://doi.org/10.1021/ja071047o).
- T.-L. Choi and R. H. Grubbs, Controlled Living Ring-Opening-Metathesis Polymerization by a Fast-Initiating Ruthenium Catalyst, *Angew. Chem., Int. Ed.*, 2003, **42**(15), 1743–1746, DOI: [10.1002/anie.200250632](https://doi.org/10.1002/anie.200250632).
- M. A. Hillmyer, S. T. Nguyen and R. H. Grubbs, Utility of a Ruthenium Metathesis Catalyst for the Preparation of End-Functionalized Polybutadiene, *Macromolecules*, 1997, **30**(4), 718–721, DOI: [10.1021/ma961316n](https://doi.org/10.1021/ma961316n).
- H. Martinez, N. Ren, M. E. Matta and M. A. Hillmyer, Ring-Opening Metathesis Polymerization of 8-Membered Cyclic Olefins, *Polym. Chem.*, 2014, **5**(11), 3507, DOI: [10.1039/c3py01787g](https://doi.org/10.1039/c3py01787g).
- G. Odian, *Principles of Polymerization*, Wiley-Interscience, Hoboken, N.J., 4th edn, 2004.



- 26 C. Tsiptsias, D. Fardis, X. Ntampou, I. Tsivintzelis and C. Panayiotou, Thermal Behavior of Poly(Vinyl Alcohol) in the Form of Physically Crosslinked Film, *Polymers*, 2023, 15(8), 1843, DOI: [10.3390/polym15081843](https://doi.org/10.3390/polym15081843).
- 27 H. E. Assender and A. H. Windle, Crystallinity in Poly(Vinyl Alcohol). 1. An X-Ray Diffraction Study of Atactic PVOH, *Polymer*, 1998, 39(18), 4295–4302, DOI: [10.1016/S0032-3861\(97\)10296-8](https://doi.org/10.1016/S0032-3861(97)10296-8).
- 28 Poly(vinyl alcohol), MW, 78000, 98% hydrolyzed (PVA 78K 98%). <https://www.polysciences.com/default/polyvinyl-alcohol-98-mol-hydrolyzed> (accessed 2024-12-04).
- 29 Elmer's Glue-All - CAMEO. [https://cameo.mfa.org/wiki/Elmer%27s\\_Glue-All](https://cameo.mfa.org/wiki/Elmer%27s_Glue-All) (accessed 2024-11-06).

