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Development of a bio-based adhesive by polymerization of Boc-protected vinyl catechol derived from caffeic acid

Catechol functionalities were applied for bio-based adhesives, which were derived from caffeic acid found in coffee beans. Using as a primer for conventional polyurethane glue, metal plates were stuck well by the adhesive.

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PAPER

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Development of a bio-based adhesive by polymerization of Boc-protected vinyl catechol derived from caffeic acid†

Shiho Tanizaki,[a] Tomohiro Kubo, [ID][a] Yosuke Bito,[b] Shigeki Mori,[b] Hiroyuki Aoki [ID][cd] and Kotaro Satoh [ID] *[a]

Catechol is a functional group that is versatile and abundant in nature, exhibiting various functions. In this report, a *tert*-butoxycarbonyl (Boc)-protected vinyl catechol (VC) monomer was synthesized from caffeic acid, which is a bio-abundant molecule found generally in coffee beans, in order to develop a bio-based adhesive. Reversible addition–fragmentation chain transfer (RAFT) polymerization of the Boc-protected VC afforded well-defined, bio-based catechol-containing polymers with controlled molecular weights and narrow molecular weight distributions. Specifically, it was facile to deprotect the pendent Boc groups quantitatively under acidic or thermal conditions to provide the desired P(VC) without requiring further purification. Consequently, the catechol-containing polymer as a primer showed highly strong adhesion against aluminum when coupled with a commercially available polyurethane adhesive.

Sustainability spotlight

Our group has focused attention on bio-derived resources for polymer materials to create a sustainable society. One of our topics is developing sustainable biobased polymers from natural biomass resources using well-defined precision polymerization techniques, which may lead to added-value and high-performance bio-based polymers. Therefore, our purpose is not only to replace petrochemical products with biomass-based ones but also to create new functional and high-performance polymers by mimicking natural functions. In this article, we applied catechol functions for adhesives, which were derived from caffeic acid found in coffee beans.

1 Introduction

In recent years, the use of renewable compounds has become desirable in the field of polymer synthesis towards the goal of developing a sustainable society.[1–4] Fortuitously, numerous plant-derived chemicals contain carbon–carbon double bonds amenable to polymerization, from which novel bio-based polymers can be prepared.[5–9] In particular, many natural aromatic compounds have styrene-type conjugated vinyl groups. For example, β-methylstyrene derivatives, which can be abundantly collected from seed oils, can be copolymerized with various monomers.[10,11] Synthesizing high-value functional aromatic polymers from bio-renewable resources is desirable because

such polymers have the potential to replace current petroleum-derived alternatives.[12]

Many naturally occurring compounds exhibit useful properties because of their innate structural features, to the extent that various bio-mimetic materials have been developed by utilizing the functional skeletons found in nature.[13–15] In particular, the catechol functional group, containing two hydroxyl groups on the benzene ring, is abundant in nature and found in substances such as mussel adhesive proteins[16] and catechins in green tea.[17] Catechols are involved in important biological functions including underwater adhesion, antioxidant properties, and antibacterial effects. In particular, the use of catechols in adhesive materials has garnered attention because of catechol's high adhesion capabilities including water-resistant adhesion.[18–24] Various types of catechol–surface interactions (*e.g.*, hydrogen bonding, π–π stacking, and coordination) could be attributed to the overall adhesion depending on the surface properties. Takahara and co-workers synthesized a light-activated adhesive by using a polymer containing caged catechol moieties with photolabile protecting groups.[25] Additionally, the same research group developed primers and additives for epoxy resins using copolymers containing catechol and glycidyl groups.[26] Similarly, others have targeted the

[a]School of Materials and Chemical Technology, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo 152-8550, Japan. E-mail: satoh@cap.mac.titech.ac.jp

[b]Konishi Co., Ltd Research & Development, Urawa Institute, 5-3-35, Nishibori, Sakura-ku, Saitama 338-0832, Japan

[c]Institute of Materials Structure Science, High Energy Accelerator Research Organization, 203-1, Shirakata, Tokai, Ibaraki 319-1106, Japan

[d]Materials and Life Science Division, J-Parc Center, Japan Atomic Energy Agency, 2-4, Shirakata, Tokai, Ibaraki 319-1195, Japan

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physical properties of catechols in the preparation of a variety of well-defined polymers.[27–31]

Catechol-containing polymers have often been synthesized by first protecting the hydroxyl groups followed by deprotection after polymerization due to catechol's redox reactivity and tendency to act as an inhibitor in radical polymerization. To avoid the initial protection step, naturally occurring piperonal[32] or petroleum-derived dimethoxystyrene[33,34] was used to synthesize catechol-containing polymers. However, harsh conditions were required to convert the methoxy groups to hydroxyl groups. Recently, we have focused on caffeic acid, a plant-derived cinnamic acid derivative found in coffee beans and other plants, as a sustainable feedstock for catechol-containing polymer synthesis. Caffeic acid was found to readily decarboxylate under basic conditions with heating to afford vinyl catechol (VC). The resulting VC can be protected in one pot using silyl or ester groups and polymerized to afford well-defined polymers.[35–37] Using the silyl-protected monomers, well-controlled polymers were obtained through living anionic or radical polymerization. Additionally, the ester-protected monomers were homopolymerized or copolymerized with various vinyl monomers using RAFT radical polymerization to afford polymers with predetermined molecular weights and narrow molecular weight distribution.[38] Although deprotection of these protected polymers proceeds quantitatively, removal of byproducts such as silanol and amide is necessary. Developing a more convenient and sustainable method that leaves no byproducts behind is highly desirable for adhesive applications because residual small molecules may weaken the catechol–surface interactions.

The aim of this study is to develop bio-based catechol polymers with a more suitable protecting group, namely the *tert*-butoxycarbonyl (Boc) group, which can be readily deprotected using acid or heat with the byproducts evolving as gas. This protecting group chemistry has been widely used in the field of photoresist materials and adhesives.[39–42] Herein, a Boc-protected VC monomer (Boc$_2$VC) was synthesized from caffeic acid and polymerized using RAFT polymerization (Scheme 1)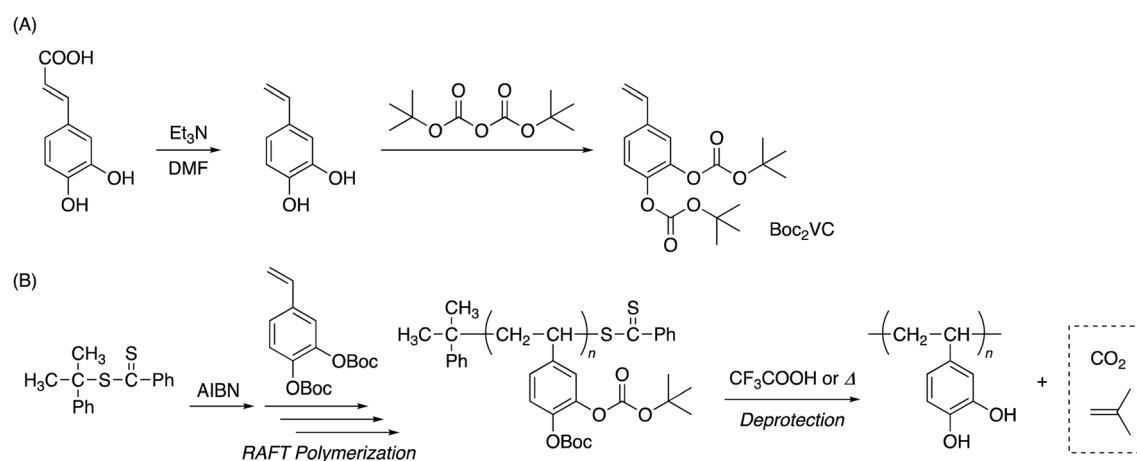. Catechol stability was evaluated at different temperatures because catechol can be oxidized to form insoluble products.[43] Consequently, the obtained catechol polymer was used as a primer for metal adhesion to highlight the utility of this synthetic approach. Combined with the primer, a commercially available polyurethane was evaluated as the adhesive against aluminum as well as its water resistance.

2 Results and discussion

2.1. Synthesis and polymerization of Boc-protected vinyl catechol (Boc$_2$VC)

In accordance with previous reports,[35–38] the decarboxylation of caffeic acid was performed in DMF in the presence of triethylamine. Then, Boc protection was carried out by directly adding di-*tert*-butyl dicarbonate in a one-pot reaction. The formation of Boc$_2$VC was confirmed by NMR analysis. The monomer was obtained by purification through a silica plug in an excellent yield. This simple approach can be readily scaled up to several tens of grams (Fig. S2 in the ESI†).

The RAFT homopolymerization of Boc$_2$VC was examined using cumyl dithiobenzoate (CDB) as the RAFT agent in ethyl acetate at 60 °C in the presence of AIBN. The reaction proceeded smoothly to obtain well-controlled polymers, of which the number average molecular weight (M_n) increased in direct proportion to the conversion and the molecular weight distributions (M_w/M_n) were narrow throughout the reaction (M_w/M_n ~1.1). In the ^{1}H NMR spectrum of the obtained P(Boc$_2$VC) after removing the residual monomer by precipitation in *n*-hexane, a small peak corresponding to the RAFT terminal dithiobenzoate group was observed at 7.8 ppm. The values of M_n (NMR) measured from the peak intensity ratio of repeat unit aromatic protons (peak *c*) and the RAFT terminal were in close agreement with the calculated values based on the feed ratio and conversion (M_n(calcd)), indicating that the polymerization was well-controlled (Fig. 1). The molecular weight determined by SEC (M_n(SEC)) was lower than M_n(calcd), which may be attributed to the difference in hydrodynamic volumes of the Boc-protected catechol polymers and the polystyrene standard. The molecular weight measured by SEC equipped with a light

Scheme 1 Synthesis of Boc$_2$VC from caffeic acid (A) and RAFT polymerization of Boc$_2$VC followed by deprotection (B).
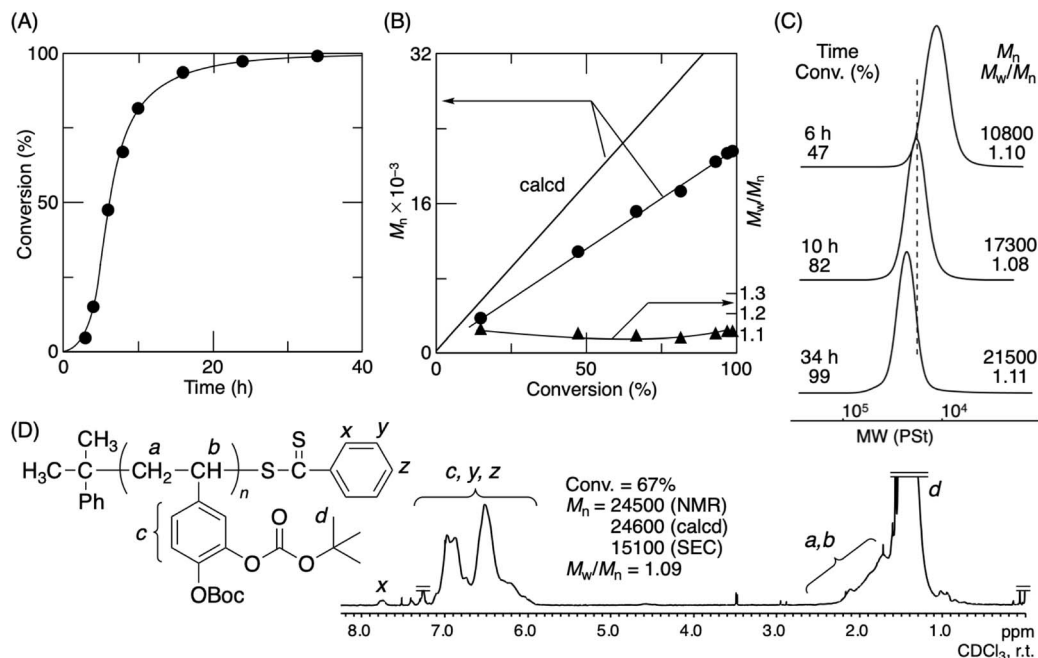
Fig. 1 Time-conversion (A), M_n(SEC) and M_w/M_n as a function of conversion (B), SEC curves (C), and ^{1}H NMR spectrum of the purified P(Boc$_2$VC) (D) for RAFT polymerization of Boc$_2$VC: [Boc$_2$VC]$_0$/[CDB]$_0$/[AIBN]$_0$ = 2000/20/5.0 mM in ethyl acetate at 60 °C.

scattering (LS) detector was closer to the calculated value (*e.g.*, M_n(calcd) = 6400, M_n(SEC) = 4900, and M_n(LS) = 6100).

To evaluate controllability, the RAFT polymerization was further explored by varying feed ratios of the monomer to the RAFT agent and by conducting a monomer addition experiment.

First, the ratio of Boc$_2$VC to the RAFT agent was varied from 25 to 1000. In all cases, the polymerization proceeded well to give polymers with a wide range of molecular weight (M_n = 5500–118,500) and relatively narrow M_w/M_n (M_w/M_n < 1.20) (Fig. 2 and Table S1†). Subsequently, a monomer addition experiment was
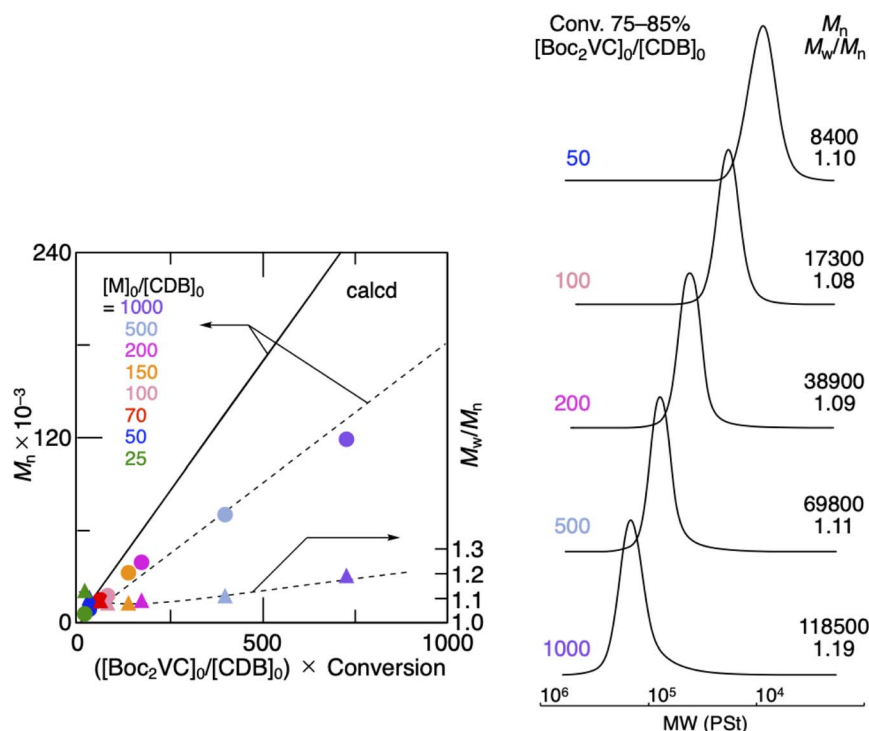

Fig. 2 SEC analysis of P(Boc$_2$VC) obtained by RAFT polymerization of Boc$_2$VC with varying feed ratios: [Boc$_2$VC]$_0$/[CDB]$_0$/[AIBN]$_0$ = 2000/2.0/ 0.50, 2000/4.0/1.0, 2000/10/2.5, 1800/12/3.0, 2000/20/5.0, 1400/20/5.0, 1500/30/7.5, 1000/40/10 mM in ethyl acetate at 60 °C.

performed. Beginning with the homopolymerization of Boc_2VC, a second portion of Boc_2VC solution was added after reaching near-complete conversion. After the addition, the consumption of the second feed of the monomer proceeded such that the M_n increased in direct proportion to the conversion and the polymerization continued to give well-controlled polymers with narrow M_w/M_n with unimodal curves in SEC analysis (Fig. S3†). These results suggest that sterically demanding Boc groups are effective in preventing termination by bimolecular radical coupling. Furthermore, very high molecular weight polymers can be obtained by free radical polymerization, further supporting the effectiveness of bulky Boc groups in inhibiting termination (Table S1 and Fig. S4†).

2.2. Deprotection of the Boc_2VC polymers

The deprotection reaction using acid was examined first by treating $P(Boc_2VC)$ with 1 equivalent of trifluoroacetic acid (TFA) per hydroxyl group in acetone at 25 °C. Gas evolution was gradually observed, and the deprotection reaction proceeded quantitatively in 2 days. ^1H NMR analysis confirmed the disappearance of peaks corresponding to the Boc groups and the appearance of catechol hydroxyl peaks (Fig. S5†).

Thermal deprotection was probed using thermal gravimetric analysis (TGA). The TGA measurement of $P(Boc_2VC)$ was performed in nitrogen, revealing a two-stage weight decrease, as indicated by the black line in Fig. 3A. Following the initial decrease at around 200 °C, the residual weight closely matched the calculated values for deprotected P(VC), assuming complete deprotection of the Boc groups. The TGA measurement was then repeated on a sample of $P(Boc_2VC)$ which was heated beforehand at 200 °C for 15 min in order to effect deprotection. As indicated by the blue line, the polymer showed a single stage of weight loss above 300 °C (the 5% weight loss temperature; T_{d5} = 340 °C), suggesting quantitative deprotection of Boc groups by heating. The complete deprotection was confirmed by the ^1H NMR analysis, based on the disappearance of methyl protons of the Boc groups (Fig. 3B). Importantly, P(VC) was obtained by thermal deprotection without requiring any purification steps, such as removal of byproducts and solvents. This synthetic method is straightforward and useful for obtaining well-defined catechol-containing polymers.

Further TGA studies were conducted at different temperatures to determine the optimal temperature and duration for deprotection. At 100 °C, the deprotection proceeded quantitatively within 5 hours, whereas the reaction did not proceed at all at 80 °C (Fig. S6†). Additionally, in DSC measurements of the protected and deprotected polymers, a significant increase in the T_g was observed (Fig. S7†) in good agreement with values previously reported for P(VC) (T_g = 190 °C),[37] further confirming the complete deprotection of Boc groups by heating.

The stability of catechol was assessed because of the known reactivity of catechols towards oxidants and to determine whether oxidation occurred during thermal deprotection. A small molecular model compound, 4-methylcatechol, and P(VC) were left exposed to air at room temperature and their structural changes were evaluated by ^1H NMR analysis (Fig. S8 and S9†). No noticeable changes were observed for either compound in 2 days, indicating that little oxidation had occurred at room temperature. Conversely, at high temperature (200 °C) in air, significant changes in the molecular weight and the shape of the SEC curves were observed for both 4-methylcatechol and P(VC) in less than 2 hours (Fig. S10†). Importantly, no significant broadening in the SEC curves was observed during the thermal deprotection in nitrogen (Fig. S11†), indicating the importance of performing the deprotection under inert conditions. Taken together, the catechol is highly stable at room temperature in air but can be rapidly oxidized at high temperature in the presence of oxygen.

2.3. Adhesion evaluation using VC polymers as a primer

Catechol groups interact strongly with aluminum mainly through coordination of two hydroxyl groups to the metallic center.[21] By utilizing this interaction, catechol-based adhesive materials have been developed for adhering to aluminum substrates.[44,45] In this work, because urethane adhesives are not effective for adhering to aluminum substrates, the use of the catechol polymer as a bio-based primer was explored to enhance adhesion strength through its interaction with the metal surface and urethane adhesive. To evaluate the effectiveness of the catechol-containing polymer as a primer, single-lap joints using aluminum substrates adhered with the urethane adhesive were prepared and measured stress–strain behavior using
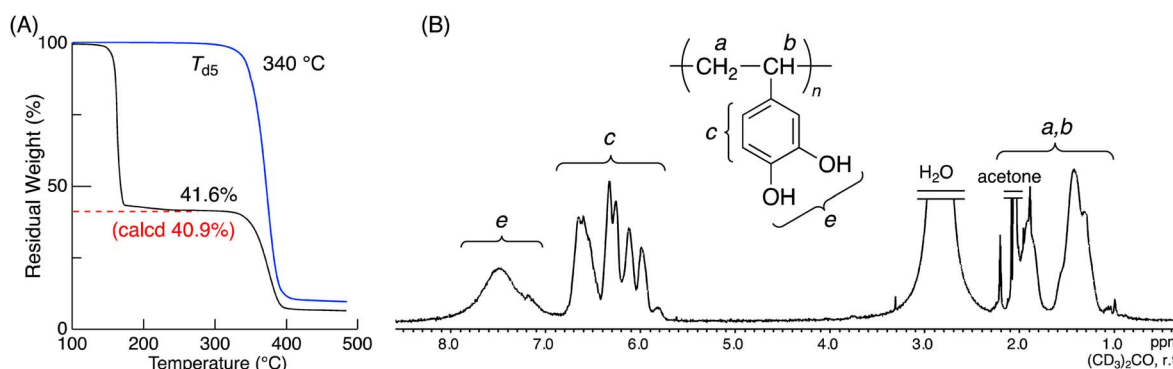

Fig. 3 TGA curves of $P(Boc_2VC)$ (black line) and $P(Boc_2VC)$ which had been heated at 200 °C for 15 min under N_2 (blue line) (A) and ^1H NMR spectra of the polymer deprotected by heat without any purification (B).

a tensile tester at room temperature (see Fig. S1†). For primer coating, the aluminum substrates were dipped in acetone solution of P(Boc$_2$VC) obtained by free radical polymerization (M_n = 1 070 000; M_w/M_n = 3.60) and heated at 200 °C for 1 hour in a vacuum oven for deprotection. This technique enabled the preparation of the aluminum plates coated using catechol-containing primers without further purification. Without the catechol primer, moderate adhesion strength (4.1 MPa) was observed, whereas with the catechol primer, significantly higher adhesion strength was observed (>15 MPa, the maximum measurement limit of the instrument) (Fig. 4A). The fracture surface was also examined to find adhesive failure for the sample without the catechol primer. Conversely, complete cohesive failure was observed for the sample using the catechol primer, confirming its effectiveness as an aluminum adhesive (Fig. 4B).

Additional adhesion tests were performed by using a series of P(Boc$_2$VC) with various M_ns obtained by RAFT polymerization (M_n = 80 100–4700; M_w/M_n < 1.20) to evaluate the effect of molecular weight on adhesion performance (Table 1 and Fig. S12†). The polymers with higher molecular weight exhibited higher adhesion strength within the range of molecular weight tested, likely due to the effects of increased chain entanglement. A water resistance test was also conducted because catechol demonstrates excellent underwater adhesion. After 1 week of immersion in water, all samples with the P(VC) primer retained their adhesive strength regardless of molecular weight, indicating the effectiveness of this bio-derived primer even in underwater environments (Fig. S13†).

In order to assess the thickness of the primer layer, the refractive indices of P(Boc$_2$VC) and P(VC) were first measured using ellipsometry (Fig. S14†). Then, the primer thickness was determined by the interference interval method using a UV-Vis spectrophotometer, a mirror-surface reflecting measurement device, and film thickness calculation software (eqn S1†). The film thickness could be increased by increasing the concentration of the polymer dip solution, though excessively high concentrations resulted in uneven primer coatings (Fig. S15†). Although the primer thickness used for adhesion tests was too thin to measure directly, the value was estimated to be 60 nm by extrapolation (dip solution: 1 wt%), suggesting high primer effectiveness at low loadings.

To probe the interaction of the catechol primer with the urethane adhesive, the reaction of catechol with components of the urethane adhesive (i.e., alcohol and isocyanate) was investigated using a model reaction. 4-Methylcatechol, diethylene glycol, and phenyl isocyanate were combined at room temperature in acetone-d_6. After 1 hour, several new peaks in the ^{1}H NMR spectrum were identified and attributed to the products of the reaction of isocyanate with alcohol or catechol (Fig. S16†). This result confirms that isocyanate reacts not only with alcohols for urethane formation but also with the catechol primer, suggesting covalent bond formation between the urethane adhesive and bio-based P(VC) primer.
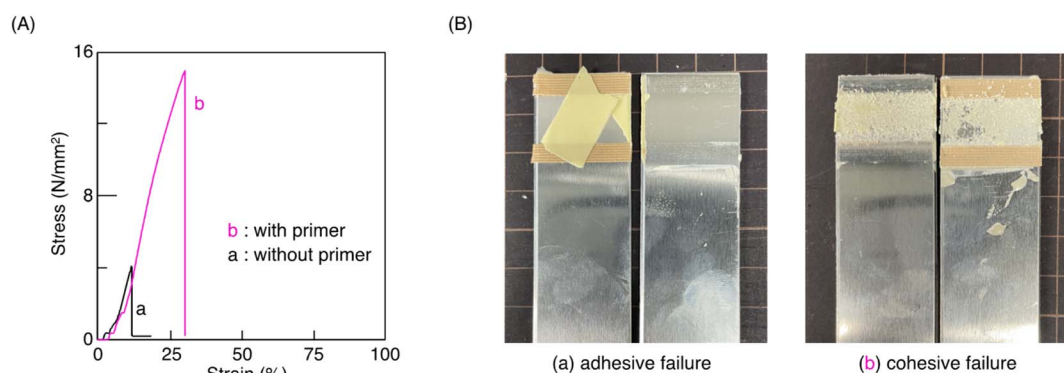

Fig. 4 Stress–strain curves of aluminum substrates adhered with urethane adhesives with or without the P(VC) primer coating (A) and photographs of fracture surfaces (B).

Table 1 Adhesion evaluation of primer-coated or non-coated aluminum plates

Entry	M_n of P(Boc$_2$VC)[a]	M_w/M_n of P(Boc$_2$VC)[a]	Max. stress[b] (MPa)	Cohesive failure[b] (%)	Max. stress after water resistance test[b] (MPa)	Cohesive failure after water resistance test[b] (%)
1[c]	—[e]	—[e]	4.07	0	—[f]	—[f]
2[c]	1 070 000	3.60	>15.0	>95	—[f]	—[f]
3[d]	80 100	1.10	15.6	>95	16.0	>95
4[d]	32 500	1.08	14.4	>95	15.5	>95
5[d]	4700	1.17	12.3	0	13.0	0

[a] Determined by SEC. [b] Average of three tests. [c] Dip solution: 1 wt%, adhesion area: 25 × 12 mm^2. [d] Dip solution: 2 wt%, adhesion area: 25 × 10 mm^2. [e] No primer used. [f] Not tested.

3 Conclusion

Boc-protected VC was obtained from caffeic acid in a one-pot and scalable reaction and polymerized *via* RAFT radical polymerization to give well-controlled polymers. The resulting polymers were deprotected quantitatively using acid or heat to afford catechol-containing polymers. These polymers were found to be highly effective when used as a primer using thermal deprotection of Boc for aluminum adhesion through the aluminum–catechol interaction as well as the bond-forming reaction between catechol and isocyanate. As a result, the following two features could be achieved from the viewpoint of sustainability. (1) The catechol group, which is a naturally-occurring functional group, could be introduced into polymers to enable the preparation of a biomimetic adhesive using a bio-based raw material. (2) The deprotection proceeded just upon heating with neither any solvent nor catalyst, releasing only gaseous byproducts, with which there is no need for further purification process for adhesive use. This straightforward and scalable approach provides an avenue for additional practical and bio-based adhesive material design by tailoring naturally available structures.

Data availability

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

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

References

1 K. Yao and C. Tang, *Macromolecules*, 2013, **46**, 1689, DOI: **10.1021/ma3019574**.

2 M. R. Thomsett, T. E. Storr, O. R. Monaghan, R. A. Stockman and S. M. Howdle, *Green Mater.*, 2016, **4**, 115, DOI: **10.1680/jgrma.16.00009**.

3 Y. Zhu, C. Romain and C. K. Williams, *Nature*, 2016, **540**, 354, DOI: **10.1038/nature21001**.

4 H. T. Nguyen, P. Qi, M. Rostagno, A. Feteha and S. A. Miller, *J. Mater. Chem. A*, 2018, **6**, 9298, DOI: **10.1039/c8ta00377g**.

5 K. Satoh, H. Sugiyama and M. Kamigaito, *Green Chem.*, 2006, **8**, 878, DOI: **10.1039/b607789g**.

6 K. Satoh, *Polym. J.*, 2015, **47**, 527, DOI: **10.1038/pj.2015.31**.

7 H. Miyaji, K. Satoh and M. Kamigaito, *Angew. Chem., Int. Ed.*, 2016, **55**, 1372, DOI: **10.1002/anie.201509379**.

8 Y. Terao, K. Satoh and M. Kamigaito, *Biomacromolecules*, 2019, **20**, 192, DOI: **10.1021/acs.biomac.8b01298**.

9 T. Nishida, K. Satoh, M. Tamura, Y. Li, K. Tomishige and M. Kamigaito, *Macromolecules*, 2022, **55**, 2300, DOI: **10.1021/acs.macromol.2c00099**.

10 K. Satoh, S. Saitoh and M. Kamigaito, *J. Am. Chem. Soc.*, 2007, **129**, 9586, DOI: **10.1021/ja0732227**.

11 K. Nonoyama, K. Satoh and M. Kamigaito, *Polym. Chem.*, 2014, **5**, 3182, DOI: **10.1039/c3py01066j**.

12 D. K. Schneiderman and M. A. Hillmyer, *Macromolecules*, 2017, **50**, 3733, DOI: **10.1021/acs.macromol.7b00293**.

13 R. R. Naik and S. Singamaneni, *Chem. Rev.*, 2017, **117**, 12581, DOI: **10.1021/acs.chemrev.7b00552**.

14 M. S. Ganewatta, Z. Wang and C. Tang, *Nat. Rev. Chem*, 2021, **5**, 753, DOI: **10.1038/s41570-021-00325-x**.

15 P. Dwivedi, K. Singh, K. Chaudhary and R. Mangal, *ACS Appl. Polym. Mater.*, 2022, **4**, 4588, DOI: **10.1021/acsapm.1c01285**.

16 J. H. Waite and M. L. Tanzer, *Science*, 1981, **212**, 1038, DOI: **10.1126/science.212.4498.1038**.

17 I. Tejero, N. González-Garcia, A. González-Lafont and J. M. Lluch, *J. Am. Chem. Soc.*, 2007, **129**, 5846, DOI: **10.1021/ja063766t**.

18 K. Kamino, *Biochem. J.*, 2001, **356**, 503, DOI: **10.1042/bj3560503**.

19 D. Kaneko, S. Wang, K. Matsumoto, S. Kinugawa, K. Yasaki, D. K. Chi and T. Kaneko, *Polym. J.*, 2011, **43**, 855, DOI: **10.1038/pj.2011.77**.

20 B. P. Lee, P. B. Messersmith, J. N. Israelachvili and J. H. Waite, *Annu. Rev. Mater. Res.*, 2011, **41**, 99, DOI: **10.1146/annurev-matsci-062910-100429**.

21 J. Saiz-Poseu, J. Mancebo-Aracil, F. Nador, F. Busque and D. Ruiz-Molina, *Angew. Chem., Int. Ed.*, 2019, **58**, 696, DOI: **10.1002/anie.201801063**.

22 B. Cheng, J. Yu, T. Arisawa, K. Hayashi, J. J. Richardson, Y. Shibuta and H. Ejima, *Nat. Commun.*, 2022, **13**, 1892, DOI: **10.1038/s41467-022-29427-w**.

23 S. Inata, H. Sogawa and F. Sanda, *Polym. J.*, 2023, **55**, 785, DOI: **10.1038/s41428-023-00770-z**.

24 J. L. Carter, C. A. Kelly and M. Jenkins, *J. Polym.*, 2024, **56**, 115–120, DOI: **10.1038/s41428-023-00846-w**.

25 J. Nishida, M. Kobayashi and A. Takahara, *ACS Macro Lett.*, 2013, **2**, 112, DOI: **10.1021/mz300524q**.

26 C.-W. Chu, Y. Zhang, T. Kubo, S. Tanizaki, K. Kojio, K. Satoh and A. Takahara, *ACS Appl. Polym. Mater.*, 2022, **4**, 3687, DOI: **10.1021/acsapm.2c00226**.

27 H. Xu, J. Nishida, W. Ma, H. Wu, M. Kobayashi, H. Otsuka and A. Takahara, *ACS Macro Lett.*, 2012, **1**, 457, DOI: **10.1021/mz200217d**.

28 C. R. Matos-Peréz, J. D. White and J. J. Wilker, *J. Am. Chem. Soc.*, 2012, **134**, 9498, DOI: **10.1021/ja303369p**.

29 N. Patil, C. Jérome and C. Detrembleur, *Prog. Polym. Sci.*, 2018, **82**, 34, DOI: **10.1016/j.progpolymsci.2018.04.002**.

30 J. Duan, W. Wu, Z. Wei, D. Zhu, H. Tu and A. Zhang, *Green Chem.*, 2018, **20**, 912, DOI: **10.1039/c7gc03323k**.

31 S. Takahashi, K. Kishikawa and M. Kohri, *Polym. J.*, 2022, **54**, 1039, DOI: **10.1038/s41428-022-00647-7**.

32 T. Ishizone, A. Mochizuki, A. Hirao and S. Nakahama, *Macromolecules*, 1995, **28**, 3787, DOI: **10.1021/ma00115a006**.

33 A. Isakova, P. D. Topham and A. J. Sutherland, *Macromolecules*, 2014, **47**, 2561, DOI: **10.1021/ma500336u**.

34 Y. Saito and H. Yabu, *Chem. Commun.*, 2015, **51**, 3743, DOI: **10.1039/c4cc08366k**.

35 H. Takeshima, K. Satoh and M. Kamigaito, *Macromolecules*, 2017, **50**, 4206, DOI: **10.1021/acs.macromol.7b00970**.

36 H. Takeshima, K. Satoh and M. Kamigaito, *ACS Sustainable Chem. Eng.*, 2018, **6**, 13681, DOI: **10.1021/acssuschemeng.8b04400**.

37 H. Takeshima, K. Satoh and M. Kamigaito, *J. Polym. Sci.*, 2020, **58**, 91, DOI: **10.1002/pola.29453**.

38 S. Tanizaki, T. Kubo and K. Satoh, *Macromol. Chem. Phys.*, 2022, **223**, 2100378, DOI: **10.1002/macp.202100378**.

39 H. Ito and C. G. Willson, *ACS Symp. Ser.*, 1984, **242**, 11, DOI: **10.1021/bk-1984-0242.ch002**.

40 C. K. Ober, F. Kafer and C. Yuan, *Polymer*, 2023, **280**, 126020, DOI: **10.1016/j.polymer.2023.126020**.

41 C. Jing, Y. Suzuki and A. Matsumoto, *Polym. Degrad. Stab.*, 2019, **166**, 145, DOI: **10.1016/j.polymdegradstab.2019.05.027**.

42 T. Sakamoto, Y. Suzuki and A. Matsumoto, *Polymer*, 2022, **280**, 125416, DOI: **10.1016/j.polymer.2022.125416**.

43 N. Schweigert, A. Zehnder and R. Eggen, *Environ. Microbiol.*, 2001, **3**, 81, DOI: **10.1046/j.1462-2920.2001.00176.x**.

44 A. Stepuk, J. G. Halter, A. Schaetz, R. N. Grass and W. Stark, *J. Chem. Commun.*, 2012, **48**, 6238, DOI: **10.1039/c2cc31996a**.

45 A. A. Putnam and J. J. Wilker, *Soft Matter*, 2021, **17**, 1999, DOI: **10.1039/D0SM01944E**.