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ORIGINAL ARTICLE

Polymers of lignin-sourced components as a facile chemical integrant for the Passerini three-component reaction

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Abstract

In this work, poly(methacrylated vanillin) (PMV) was investigated for its reactivity in multicomponent reactions as a reactive polymer that can be sourced from lignin-based components. To achieve sustainable polymer chemistry, the PMV reactivity in a Passerini three-component reaction (Passerini-3CR) was investigated because the reactants in the Passerini-3CR can be abundantly sourced from biobased compounds. First, the Passerini-3CR of the PMV in solution phases revealed that the PMV pendant aldehydes can be converted into the corresponding α-acyloxy amides with >90% conversions under the optimized conditions. Taking advantage of this high reactivity of PMV, its immobilized cellulose fabric (Cell-*g*-PMV), a wood biomass-sourced organic hybrid, was subjected to the Passerini-3CR. Although the aldehydes were not completely converted, the PMV segments surrounding the fabric surfaces successfully reacted via the Passerini-3CR to engraft carboxylic acid and isocyanide components on the cellulose-based fabrics.

Introduction

Along with rapidly developing material science, functionalized fabrics, or textiles have seen an increasing demand from a wide range of interdisciplinary sciences because they serve as important components in material fabrication processes [1, 2]. Thus, hybrid materials or surface-modified materials play an indispensable role because the material properties can be guaranteed by the matrix constituents, and the surface characteristics can be tuned by the surface-anchored segments. To fabricate functional materials, matrix fabrics are therefore subjected to surface modification reactions to engraft the desired functionalities on their surfaces. From the perspective of green chemistry, there is a need for the maximum utilization of biosourced components considering the current stream in polymer and material sciences [3–5]. In this context, the application of biosourced components both as a matrix and surface segment should comply with the requirements of sustainable chemistry.

Consequently, we successfully fabricated biomass-sourced organic hybrid materials using a radiation-induced graft polymerization technique and subsequent surface multicomponent reaction (MCR) [6–11]. Precisely, cellulose serves as a matrix fabric, and lignin-sourced methacrylated vanillin was graft-polymerized from the matrix cellulose to anchor poly(methacrylated vanillin) (PMV) on the matrix surface (Cell-*g*-PMV), which realized the recombination of wood-biomass-sourced components. It should be noted that the obtained biomass-sourced organic hybrid allowed surface modification based on the feasible MCRs of the surface aldehyde groups of the PMV segments [12]. As a representative MCR for surface modification, the Kabachnik-Fields three-component reaction (KF-3CR) was employed for Cell-*g*-PMV. This resulted in feasible engraftment of the desired aromatic amines and phosphites on the matrix surfaces, resulting in the formation of α-amino phosphonate units. Although this polymeric transformation allowed engraftment of the desired functional units on the Cell-*g*-PMV, there is a drawback of this process

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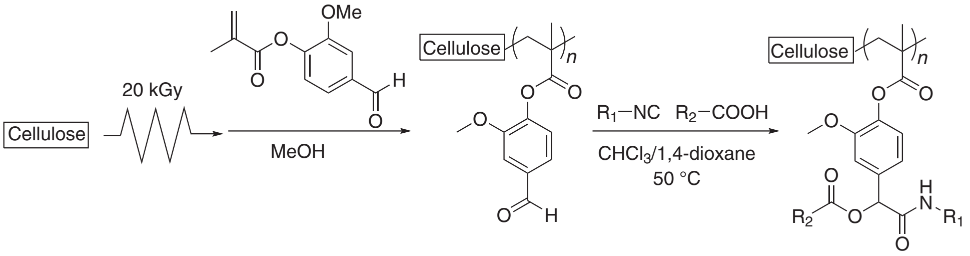
regarding green chemistry. Critically, the surface modification based on the KF-3CR involves the use of aromatic amines and phosphites as the reactants. Since natural systems rarely produce aromatic amines and phosphites, their employment in the functionalization of Cell-*g*-PMV can substantially lead to a decrease in the sustainability of the entire process. To increase the overall sustainability of Cell-*g*-PMV functionalization, the surface modification step should, therefore, employ an efficient reaction and bioprocessable components. Given that carboxylic acids and amines are produced through a wide range of bioprocesses, their application should result in an increased green ecosystem. Among the wide range of MCRs applicable in polymer chemistry [13–26], the Passerini three-component reaction (Passerini-3CR) is an ideal process because it is a reaction among aldehydes, carboxylic acids, and isocyanides [27, 28]. Here, carboxylic acids can be abundantly sourced from nature, and isocyanides can be prepared from amines that can also be obtained abundantly from nature. From our extensive literature review, the Passerini-3CR of a PMV segment both in solution and on material surfaces has not been addressed in detail.

In this work, we aimed to accomplish the Passerini-3CR modification of Cell-*g*-PMV, which can lead to sustainable surface chemistry of Cell-*g*-PMV. Hence, the Passerini-3CR of a PMV was precisely investigated, and the Cell-*g*-PMV was subjected to the reaction to modify the surface of the PMV segments (Scheme 1).

Results and discussion

Precise insight into the Passerini-3CR of PMV

As mentioned in the introduction, we focused on the employment of the Passerini-3CR for the surface modification of Cell-*g*-PMV. Thus, the reactivity of PMV in the Passerini-3CR was first precisely investigated in the solution phase, which enabled a detailed discussion of the reactions. Therefore, RAFT-prepared PMV was subjected to the Passerini-3CR with 1-adamantyl isocyanide and 1-hexanoic acid as the model reactants. Precisely, the PMV was reacted in $CHCl_3$ at 50 °C for 40 h, where the reactant concentration of $[CHO]_0/[NC]_0/[COOH]_0$ was set as 1/3/3. ^1H NMR measurements of the obtained polymer were conducted and are presented in Fig. 1. High conversion of PMV aldehyde was proven by the significant decrease in the peak at 9.9 ppm in the ^1H NMR spectra of the prepared



Scheme 1 Representation of the radiation-induced graft polymerization of methacrylated vanillin and the solid-state Passerini-3CR with isocyanides and carboxylic acids

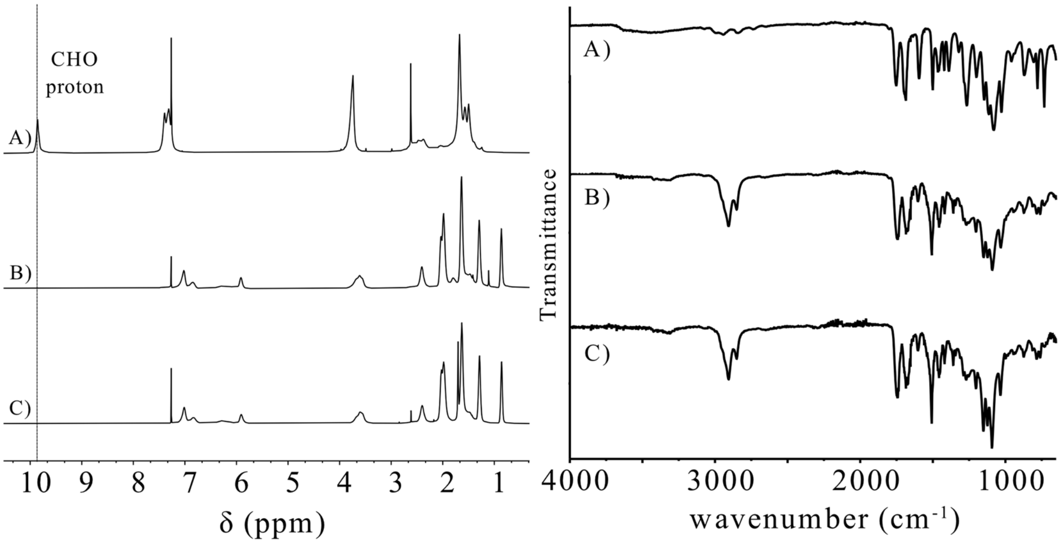


Fig. 1 ^1H NMR (left) and ATR-mode FT-IR (right) spectra of PMV (**A**) before and (**B**) after the Passerini-3CR with 1-adamantyl isocyanide and 1-hexanoic acid. (**C**) Corresponding model polymer sample prepared via radical polymerization of the model monomer

polymer (Fig. 1). Conversely, peaks of 1-adamantyl isocyanide and 1-hexanoic acid were observed and are depicted in Fig. 1, revealing that the PMV aldehyde groups were converted into the corresponding α-acyloxy amides via the Passerini-3CR. In addition to the ^{1}H NMR analysis, FT-IR analyses revealed that the amide band of the product polymer after the Passerini-3CR was observed in the range of 1640–1710 cm^{-1} (Fig. 1), indicating amide generation via the Passerini-3CR. In addition, both the ^{1}H NMR and FT-IR spectra of the obtained polymer were consistent with those of the model polymer synthesized via the free radical polymerization of the corresponding methacrylate monomer (Fig. 1). This indicated that the Passerini-3CR of the PMV proceeded with an efficient conversion. In addition, SEC measurements of PMVs before and after the Passerini-3CR revealed that the molecular weight of PMV increased due to the facile Passerini-3CR conversion, and no perceptible side reactions, such as cross-linking, were observed, as depicted in Fig. 2.

To apply the Passerini-3CR in efficient surface chemistry, precise insight into the Passerini-3CR is required. Thus, the effects of the reaction time, reactant concentrations, and solvents on the Passerini-3CR of the PMVs were investigated. First, a kinetic experiment for the reaction was conducted with 1-adamantyl isocyanide and 1-hexanoic acid as model reactants. PMV was reacted in $CHCl_3$ at 50 °C, where the reactant concentration of $[CHO]_0$ and the reactant ratio of $[CHO]_0/[NC]_0/[COOH]_0$ were set as 0.63 $\mathrm{mol{\cdot}L^{-1}}$ and 1/3/3, respectively, as depicted in Fig. 3. As revealed in Fig. 3, the PMV aldehyde conversion rapidly reached ~80% 2 h immediately after reaction initiation, and the aldehyde conversion gradually increased to completion. The Passerini-3CR was expected to involve a four-component transition state comprised of three reactants and a carboxylic acid [29, 30], which rationally requires the reactants to be dense enough to ensure the four-component transition state. Together with the kinetic features of the Passerini-3CR, the effects of the reaction conditions were investigated, as summarized in Table 1. Although a decrease in the reactant stoichiometry led to lower aldehyde conversions, the impact was unclear (runs 1–4, Table 1). This can be attributed to accelerated hydrogen bonding among the reactants due to the loss of molecular mobility in the viscous reaction solutions since the PMV concentration demonstrated a larger impact on the reaction conversions (runs 5 and 6, Table 1). Considering the reaction mechanism discussed above, the solvent polarity played a crucial

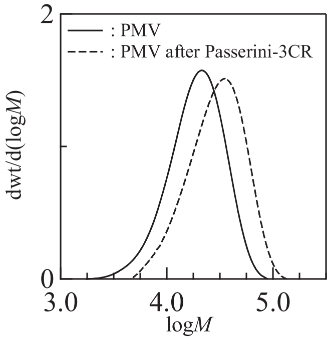


Fig. 2 SEC charts of PMV before and after the Passerini-3CR with 1-adamantyl isocyanide and 1-hexanoic acid

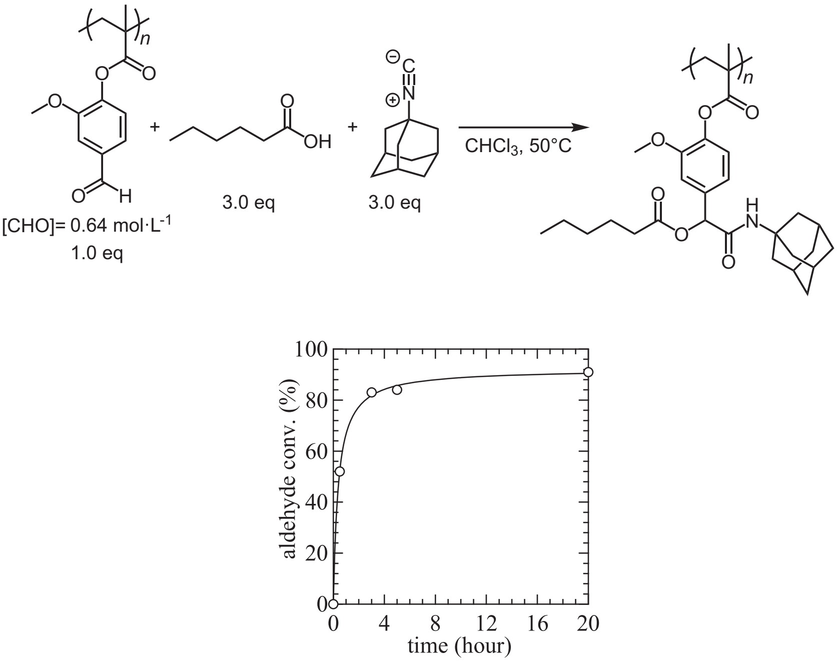
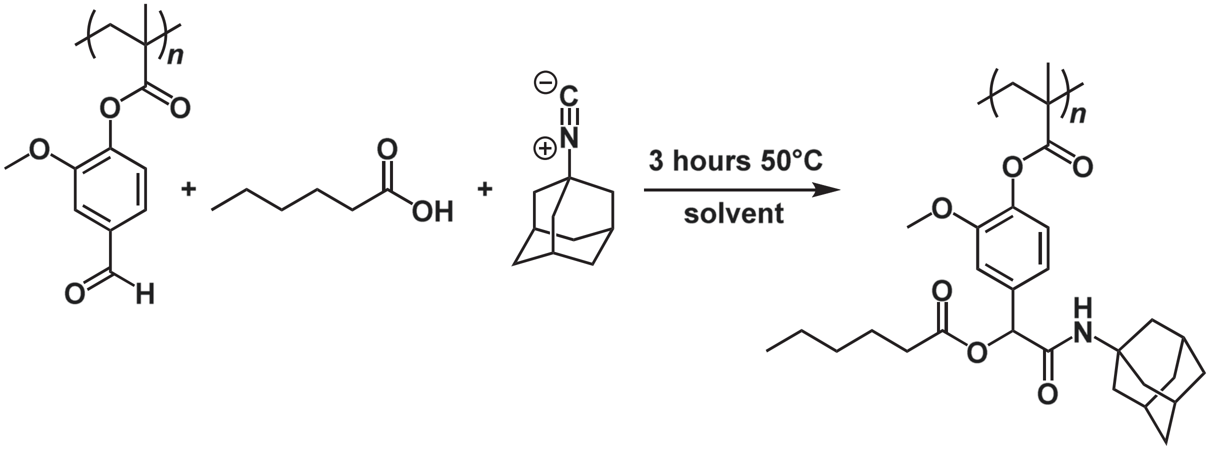


Fig. 3 Kinetic results for the Passerini-3CR of PMV with 1-adamantyl isocyanide and 1-hexanoic acid

Table 1 Effects of the reaction conditions on the Passerini-3CR of PMV



Entry	Solvent	$[CHO]_0$ [mol·L^{-1}]	$\frac{[COOH]_0}{[CHO]_0}$	$\frac{[NC]_0}{[CHO]_0}$	Conv. (%)[a]
1	$CHCl_3$	0.6	3.0	3.0	83
2	$CHCl_3$	0.6	1.2	3.0	60
3	$CHCl_3$	0.6	3.0	1.2	66
4	$CHCl_3$	0.6	1.2	1.2	53
5	$CHCl_3$	1.3	1.2	1.2	74
6	$CHCl_3$	0.3	1.2	1.2	49
7	DMF	0.6	3.0	3.0	82
8	DMSO	0.6	3.0	3.0	55
9	1,4-dioxane	0.6	3.0	3.0	87

[a] Determined by ^1H NMR measurements in $CDCl_3$

role in the Passerini-3CR of PMV, where an increase in polarity led to a remarkable decrease in the reaction efficiency of the Passerini-3CR (runs 7–9, Table 1), reflecting the importance of hydrogen bonding in the Passerini-3CR of PMV. Conclusively, the biosourced polymer PMV was feasibly subjected to the Passerini-3CR under mild conditions preferably in aprotic solvents, and this can realize high PMV aldehyde conversions to produce the corresponding polymers featuring α-acyloxy amides.

The Passerini-3CR of the biosourced organic hybrids

Supported by the feasible Passerini-3CR of PMVs, we thus targeted Passerini-3CR of Cell-*g*-PMV, which was prepared using the radiation-induced graft polymerization technique on cellulose fabrics. For the feasible Passerini-3CR surface modification, high reactant concentrations in aprotic solvents were clearly indicated by precise investigations in the solution phase. Therefore, Cell-*g*-PMV was subjected to the surface Passerini-3CR in $CHCl_3$ with 1-adamantyl isocyanide and 1-hexanoic acid. Although the reaction conditions were the same as those of the solution phase reaction, the surface Passerini-3CR did not proceed smoothly. This low reactivity for Cell-*g*-PMV in $CHCl_3$ was presumably attributed to the incompatibility of apolar $CHCl_3$ with the hydrophilic cellulose surfaces. Based on this assumption, 1,4-dioxane was selected as a cosolvent since it is miscible with water but maintains a low dielectric constant; thus, it revealed a comparable reactivity with $CHCl_3$. This should sufficiently enhance the compatibility of the reactants with cellulose surfaces, and the impact on the Passerini reactivity can be neglected. Therefore, Cell-*g*-PMV was subjected to the surface Passerini-3CR in $CHCl_3$/1,4-dioxane. As expected, the Passerini-3CR on Cell-*g*-PMV proceeded smoothly, as indicated by the FT-IR (Fig. 4) and SEM-EDX (Figs. 5 and 6) measurements of the Cell-*g*-PMV fabrics before and after the Passerini-3CR, where the aldehyde conversion was determined to be 41%. Of note, the FT-IR spectrum of Cell-*g*-PMV after the Passerini-3CR showed that the Passerini-modified fabrics would essentially be free from contamination by the reactants. Although the

FT-IR spectrum of Cell-*g*-PMV after the Passerini-3CR could not provide clear insight into the reaction profile, scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) measurements of Cell-*g*-PMV after the Passerini-3CR revealed a distinct peak of nitrogen atoms that can be rationally sourced from isocyanide components, whereas the initial Cell-*g*-PMV showed no peaks of nitrogen atoms, as depicted in Fig. 5. In addition, the nitrogen atom content was estimated to be 1.9 wt% by SEM-EDX measurement, which gave reasonable agreement with the theoretical value of 2.8 wt% for the Passerini-modified monomeric unit. Considering that the PMV segments of Cell-*g*-PMV partially penetrated the fabric cores, the Passerini-3CR reactivity was thus expected to be suppressed, which can result in rather limited conversions of the PMV aldehydes. Nevertheless, the Passerini-3CR feasibly occurred at least on the surface of Cell-*g*-PMV, which allowed the installation of carboxylic and isocyanide components on the biosourced organic hybrids.

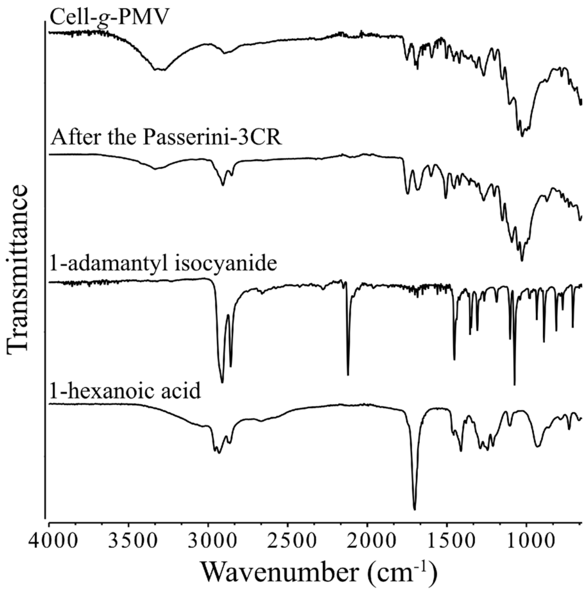


Fig. 4 ATR mode FT-IR spectra of Cell-*g*-PMV before (upper) and after (lower) the Passerini-3CR with 1-adamantyl isocyanide and 1-hexanoic acid

To showcase a proof of concept, biorenewable reactants were preliminarily employed for the surface modification of Cell-*g*-PMV. Specifically, *N*-Boc-L-methionine and ethyl isocyanoacetate were selected as a methionine-based carboxylic acid and a glycine-based isocyanide, respectively, both of which can be synthesized from amino acids. In the same manner as the model surface functionalization, the amino acid-derived compounds reacted with the Cell-*g*-PMV surface with 50% aldehyde conversion via the Passerini-3CR pathway, as indicated by the peaks of nitrogen and sulfur atoms measured in the SEM-EDX spectrum (Fig. 7). Notably, the development of the sulfur peak would further lend support to the feasible surface Passerini-3CR on Cell-*g*-PMV. Based on our approach, the fully biosourced fabrication of functional materials can be achieved without the use of additional catalysts or activa-

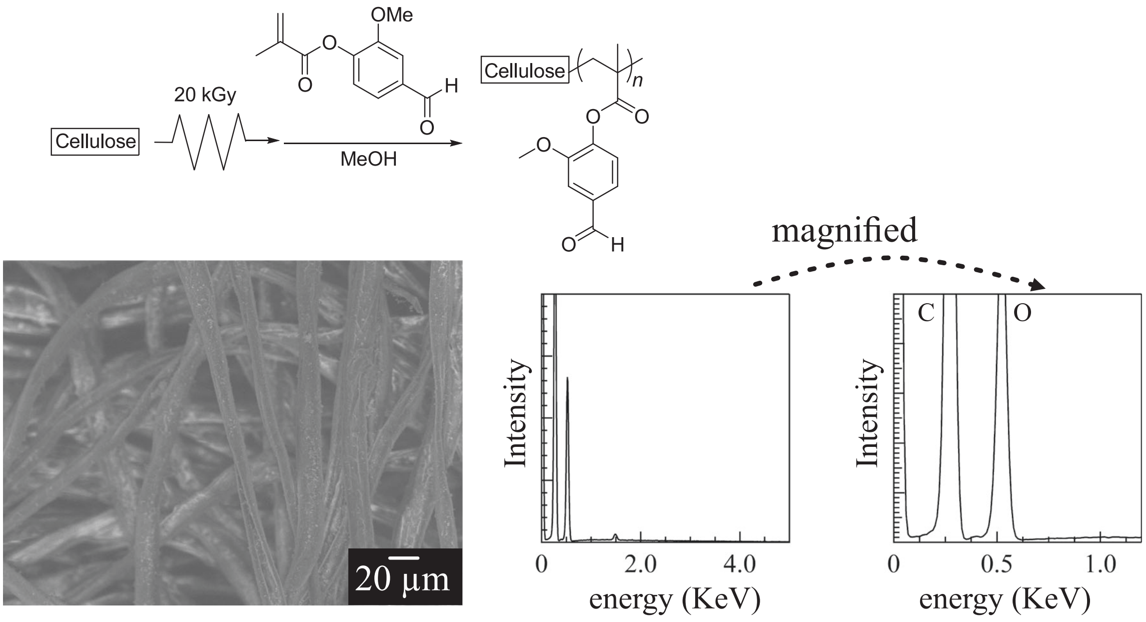


Fig. 5 SEM image and the associated EDX spectrum of the Cell-*g*-PMV

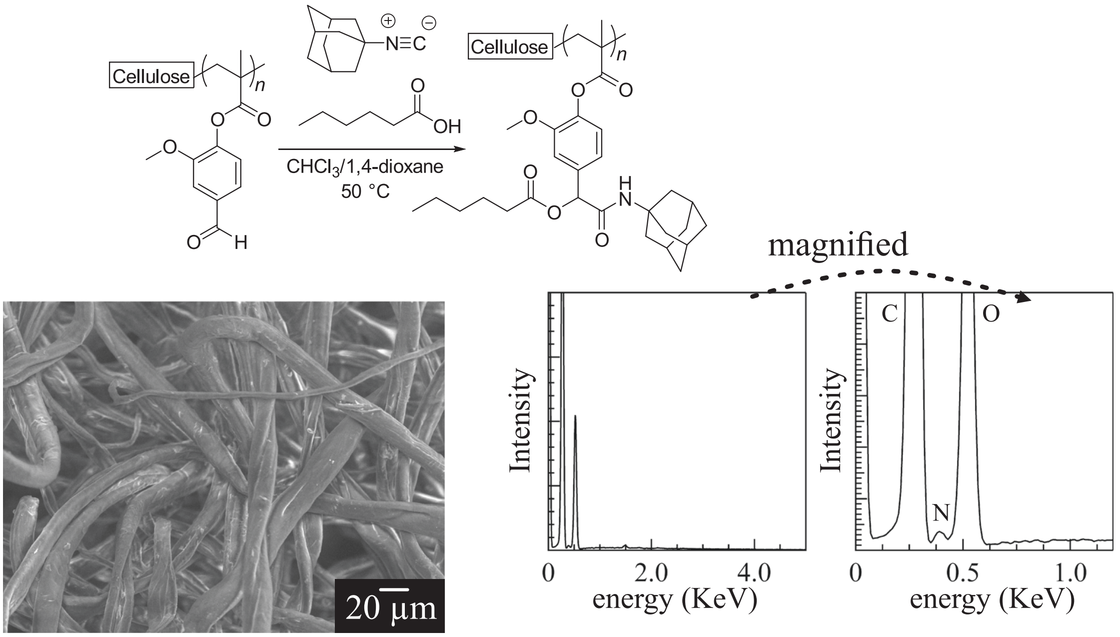


Fig. 6 SEM image and the associated EDX spectrum of Cell-*g*-PMV after the Passerini-3CR with 1-adamantyl isocyanide and 1-hexanoic acid

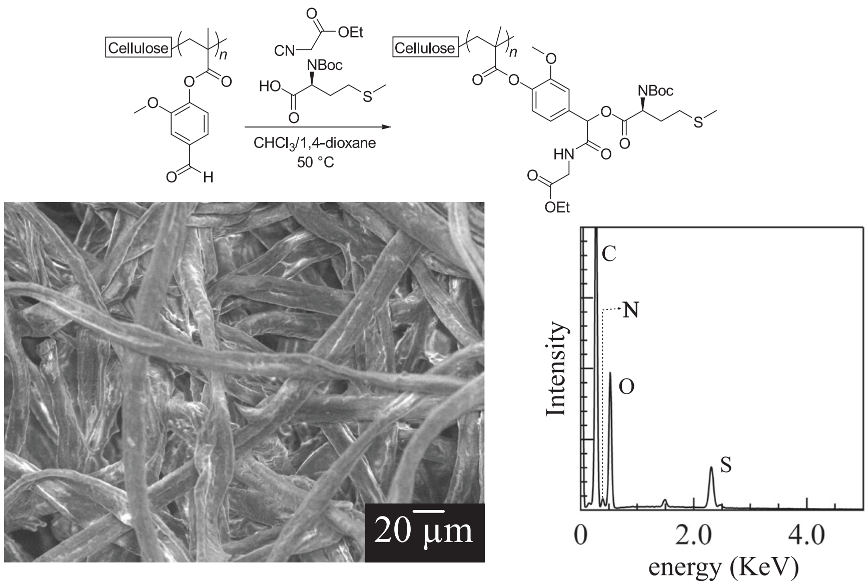


Fig. 7 SEM image and the associated EDX spectrum of Cell-*g*-PMV after the Passerini-3CR with *N*-Boc-L-methionine and ethyl isocyanoacetate

tors, taking advantage of the high compatibility between MCR and biobased compounds.

Conclusions

In this manuscript, we have successfully investigated PMV reactivity in the Passerini-3CR in both solution and solid phases. The lignin-derived PMV exhibited high compatibility with the Passerini-3CR in producing the corresponding polymers with pendant α-acyloxy amides. Taking advantage of PMV reactivity in the Passerini-3CR, complete biosourced surface modification was preliminarily performed on Cell-*g*-PMV using α-amino acid-based compounds, which essentially allowed the installation of α-amino acid-sourced molecules via the surface Passerini-3CR. Since all of the employed components, including cellulose fabric, surface-anchored PMV, and surface-modifying reagents, were biobased, this research provides insight into the use of biosourced compounds for the fabrication of functional materials.

Experimental section

Materials

2,2'-Azobis(isobutyronitrile) (AIBN) was purchased from the FUJIFILM Wako Pure Chemical Co., Ltd. and used after recrystallization from MeOH. All other chemicals were commercially sourced and used without further purification unless otherwise stated. MV was synthesized according to a published protocol [11, 12]. Although Cell-*g*-PMV was prepared according to the published protocol, the preparation guidelines are briefly documented in the synthetic section below [12].

Instruments

All NMR spectra were recorded in deuterated solvents by a Bruker 500 MHz FT-NMR spectrometer, and the chemical shifts (δ) were given in ppm with either the solvent peak or TMS as the internal standard. The SEC measurements were performed in THF at 45 °C at a flow rate of 0.5 mL·min^{-1} on a Waters Advanced Polymer Chromatograph (APC) embedded with three columns (4.6 ×150 mm ACQUITY APC columns, XT 45 1.7 μm, XT 200 2.5 μm, and XT 450 2.5 μm). The M_n and $Đ$ values of the polymers were calculated according to a PSt calibration. The IR spectra were recorded by an Agilent Cary 630 or PerkinElmer FT-IR equipped with an ATR measurement unit. Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) was performed with the spectrometer attached to a HITACHI SU3500 microscope. The sample was attached to the holder with carbon tape. The column purifications were carried out using a single channel automated flash chromatography system (Smart Flash EPCLC AI-580S, Yamazen). The optimized solvent conditions for column purification were determined by EPCLC AI-580S.

Synthesis

Synthesis of the model monomer (MV-AA)

MV (250 mg, 1.14 mmol), hexanoic acid (158 mg, 1.36 mmol) and 1-isocyanoadamantane (220 mg, 1.36 mmol) were dissolved in $CHCl_3$ (0.88 mL), and the mixture was stirred at 50 °C for 24 h. After reaction completion, the reaction solution was extracted twice with CH_2Cl_2, washed twice with sat. $NaHCO_3$ aq and washed once with water. The combined organic layer was dried over $MgSO_4$. The obtained crude product was purified by column chromatography and subsequent recrystallization to afford a white powder model compound (MV-AA).

Yield (241 mg, 42.4%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 – 6.92 (m, 3H), 6.34 (s, 1H), 5.95 (s, 1H), 5.83 – 5.66 (m, 2H), 3.83 (s, 3H), 2.51 – 2.35 (m, 2H), 2.17 – 1.91 (m, 12H), 1.68 (s, 8H), 1.40 – 1.27 (m, 4H), 0.91 – 0.88 (m, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 172.01, 167.01, 165.32, 151.35, 140.34, 135.55, 134.78, 127.46, 122.99, 119.53, 112.06, 74.95, 56.06, 52.27, 41.51, 36.29, 34.32, 31.30, 29.44, 24.62, 22.38, 18.51, 13.97. Anal. Calcd for $C_{29}H_{39}NO_6$ (497.632): C, 70.00; H, 7.90; N, 2.81; Found: C, 70.16; H, 7.82; N, 2.83.

Synthesis of the model polymer (PMV-AA)

MV-AA (200 mg, 0.40 mmol) and AIBN (0.66 mg, 4.0 μmol) were dissolved in DMSO (0.40 mL), and the obtained mixture was degassed with Ar for 10 min. The reaction solution was then stirred at 70 °C for 24 h. After completion of the reaction, the reaction solution was diluted with $CHC1_3$ and added dropwise to MeOH for purification. The obtained powder was dried under reduced pressure to obtain a white powder of the target polymer (PMV-AA).

Yield (134 mg, 67.2%) SEC (THF): 43.0 × 10^3 g·mol^{-1}

Synthesis of PMV

A 1,4-dioxane/DMSO mixed solution (v/v = 1/1, 9.6 mL) of MV (5.1 g, 22.7 mmol), methyl 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoate (100 mg, 0.227 mmol), and ABCN (5.1 mg, 0.027 mmol) was degassed with Ar for 20 min and then stirred for 21 h in an oil bath preheated at 100 °C. After polymerization completion, the reaction solution was diluted with $CHCl_3$ and added dropwise to MeOH. The obtained solid was dried to afford white powder.

Yield (2.94 g, 57.8%) SEC (THF): 15.7 ×10^3 g·mol^{-1} and $Đ = 1.41$

The Passerini-3CR of PMV

A typical procedure for the Passerini-3CR post-modification of PMV is as follows: PMV (100 mg, [CHO] = 0.46 mmol), hexanoic acid (158 mg, 1.36 mmol) and 1-isocyanoadamantane (219 mg, 1.36 mmol) were added to a vial and dissolved in $CHCl_3$ (0.72 mL). After the reaction mixture was stirred at 50 °C for 40 h, the reaction solution was precipitated dropwise in MeOH. The obtained powder was dried under reduced pressure to afford the target polymer.

Yield (157 mg, 69.7%) SEC (THF): 23.6 × 10^3 g·mol^{-1} and $Đ = 1.45$

Radiation-induced graft polymerization of MVs onto cellulose (Cell-g-PMV)

A typical procedure for Cell-*g*-PMV preparation is as follows: cellulose (Cell) nonwoven fabric (2 × 2 cm) was sealed with an oxygen scavenger, and an electron beam (250 KeV, 1.9 mA) was used to irradiate the fabric with a 20 kGy dose. Next, MV (350 mg) was dissolved in MeOH (3.5 mL), and the solution was degassed with N_2 for 10 min to prepare a polymerization solution. After the cellulose fabric irradiated with the electron beam was placed in a Schlenk tube under an inert atmosphere, the MV solution was added into the Schlenk tube. The polymerization solution was then heated at 60 °C for 3 h. After completion of the reaction, the nonwoven fabric was washed with 1,4-dioxane and $CHCl_3$ three times and dried at 60 °C overnight to obtain white nonwoven Cell-*g*-PMV.

Grafting degree (GD, $\frac{W_g - W_0}{W_0} \times 100$, where W_0 and W_g are the weights before and after graft polymerization, respectively): 52%

Surface Passerini-3CR of cell-g-PMV

A typical procedure for the surface Passerini-3CR is as follows: Cell-*g*-PMV ([CHO] = 1.0 eq), hexanoic acid (200 eq) and 1-isocyanoadamantane (100 eq) were added to a vial and dissolved in $CHCl_3$/1,4-dioxane (1/1 (v/v), 0.3 mL), and then, Cell-*g*-PMV was immersed in the solution. The reaction mixture was stirred at 50 °C for 48 h. After completion of the reaction, the fabric was washed with 1,4-dioxane and $CHCl_3$ three times each and dried under reduced pressure overnight. The reaction conversion was determined by gravimetry.

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Compliance with ethical standards

Conflict of interest We declare that there are no conflicts of interest to this work.

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