

**Dehydrogenative silylation of cellulose in ionic liquid**

Journal:	<i>Green Chemistry</i>
Manuscript ID	GC-COM-08-2023-002894
Article Type:	Communication
Date Submitted by the Author:	04-Aug-2023
Complete List of Authors:	Hirose, Daisuke; Kanazawa University, Graduate School of Natural Science and Technology Kusuma, Samuel; Kanazawa University, Graduate School of Natural Science and Technology; University Negeri Semarang, Department of Chemistry, Faculty of Mathematics and Natural Science Yoshizawa, Akina; Kanazawa University, Institute of Science and Engineering Wada, Naoki; Kanazawa University, Institute of Science and Engineering Takahashi, Kenji; Kanazawa University, Institute of Science and Engineering

Dehydrogenative silylation of cellulose in ionic liquid

Daisuke Hirose,^{a,*} Samuel Budi Wardhana Kusuma,^{a,b} Akina Yoshizawa,^a Naoki Wada^a and Kenji Takahashi^{a,*}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

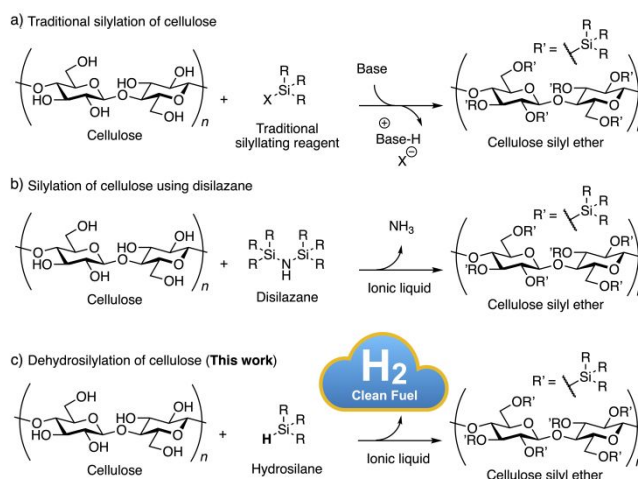
www.rsc.org/

A new homogenous silylation method of cellulose is developed by mixing it with monohydrosilane in an ionic liquid. In this concise reaction with high atom economy, the ionic liquid acts as both the solvent and catalyst, and the only formal by-product generated is the clean fuel of molecular hydrogen.

Bio-based materials for mitigating the environmental issues should be synthesized using methods with minimal environmental burden.¹⁻² In recent years, the use of lignocellulosic biomass including polysaccharides typified by cellulose as a substitute for petroleum resources has been recommended.³ The silylation of hydroxyl group on polysaccharides is widely used to change the solubility and intermolecular interaction of polymers to prepare thin bio-based films^{4,5} and gas-permeable membranes,⁶ as well as for protection to aid in regioselective modification.^{7,8} The silylation of hydroxyl groups in the polysaccharides has mainly been performed using the silylating reagents with leaving groups including monohalosilanes such as monochlorosilane (Scheme 1a).⁹ Numerous studies have reported the combination of reaction solvents and appropriate silylating reagents to perform these polysaccharide modifications in a homogenous system. However, it is necessary to use excess amounts of basic compounds such as pyridine and liquid ammonia as well as unique solvent systems such as dimethylacetamide (DMAc)/LiCl.¹⁰ In addition, the waste derived from the leaving groups of the silylating reagents is generated, and an additional base is needed in the cases where acidic waste is produced. Thus, there is room for improvement in terms of resource

conservation and handling during the silylation of polysaccharides.¹¹

Cellulose has very low solubility in common solvents because of the presence of hydrogen bonding networks derived from the hydrogen bonds between the hydroxyl groups at the 2, 3 and 6 positions, which has been an obstacle in the development of cellulose-based materials based on chemical modification.¹⁰ Ionic liquids (ILs)¹² are the molten ionic compounds that were reported at the beginning of the 21st century, and can dissolve poorly soluble polysaccharides such as cellulose.^{13,14} Since then, the development of methods for modifying cellulose to prepare bio-based materials in ILs has been promoted.^{10,15-17} In addition to esterification and etherification, the silylation of cellulose has been developed from an early stage, and a wide range of silylating reagents such as disilazane^{18,19} and monochlorosilane²⁰ can be employed (Scheme 1b). However, as described above, issues including the



Scheme 1. Schematic of cellulose silylation: (a) traditional silylation using activated silylating reagents and (b) that using disilazane and (c) monohydrosilane in an ionic liquid acting as a catalyst and solvent (this work).

^aGraduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan. ^bDepartment of Chemistry, Faculty of Mathematics and Natural Science, Universitas Negeri Semarang, Semarang City, Central Java 50229, Indonesia. E-mail: dhirose@se.kanazawa-u.ac.jp, ktkenji@staff.kanazawa-u.ac.jp

† Electronic Supplementary Information (ESI) available: Characterization of cellulose silyl ethers. See DOI: 10.1039/x0xx00000x

COMMUNICATION

Journal Name

generation of harmful wastes such as hydrogen chloride and ammonia gases are encountered, which often require additional neutralizing reagents such as bases and acids.

In recent years, dehydrogenative silylation using hydrosilane has attracted considerable attention as an environmentally friendly reaction, particularly from the viewpoint of atom economy, where molecular dihydrogen gas is generated as the only theoretical by-product.²¹ However, unlike the conventional silylating reagents containing a leaving group, the reaction does not proceed solely with hydrosilane, and appropriate catalysts have been developed. Mainly, the transition metal catalysts such as Rh, Ru, Ir, Co, Mn, and Fe, which exhibit excellent catalytic activities, have been developed,²²⁻²⁴ and alkali metals²⁵⁻³² and organocatalysts³³⁻³⁹ have also been reported in recent years. Even the carbonate salts have been found to act as catalysts,^{26, 37, 40}; according to Corriu's pioneering research in the 1970s, the dehydrogenative silylation of alcohol proceeds in alkyl ammonium carboxylate (molten dodecylammonium propionate).²⁵ However, the reactivity with monohydrosilanes, which can be used for polysaccharide (polyol) modification without crosslinking, has not been investigated in the Corriu's report. Corriu also reported the dehydrogenative silylation of alcohol with other metal carboxylate salts; however, an extremely high temperature (140–180 °C), sufficient to decompose the cellulose backbone, was required to afford the desired silyl ethers.^{26, 27}

In this study, the dehydrogenative silylation reaction between cellulose and monohydrosilane in an IL containing a carboxylate anion focused on the 1,3-substituted imidazolium acetate, a well-known solvent for cellulose, is described (Scheme 1c).

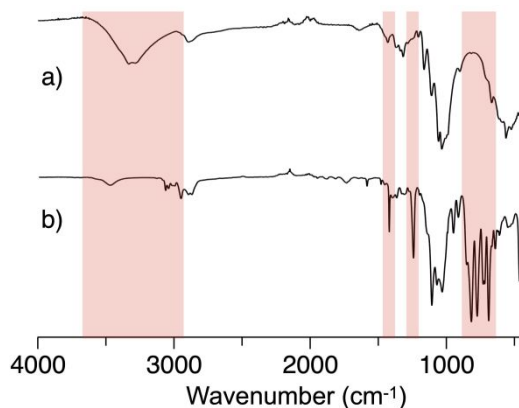


Figure 1. ATR-mode FT-IR spectra of (a) original cellulose and (b) the resulting cellulose dimethylphenylsilyl ether (DS = 2.57) in Scheme 2.

It has been reported that a mixed solvent system of **1-ethyl-3-methylimidazolium acetate (EmimOAc)** and dimethylsulfoxide (DMSO) dissolves cellulose⁴¹⁻⁴³. Equimolar amount of dimethylphenylsilane (**1**: PhMe₂SiH) to the hydroxyl groups on cellulose was added to a solution of cellulose dissolved in a mixture of EmimOAc/DMSO (1/20, molar ratio) and heated at 60 °C under an Ar atmosphere for 18 h (Scheme 2). This solution was in a homogenous state from the start to the end, indicating that EmimOAc acted as a solvent for cellulose in this system. After the reaction, the resulting polymer was recovered as a white fibrous solid from the reaction mixture by reprecipitation in the MeOH. The IR data of the obtained cellulose derivatives showed absorption bands at 3100–2900 cm⁻¹, corresponding to the C–H bond, and at approximately 1430, 1250 and 900–600 cm⁻¹, corresponding to the silyl ether group (Figure 1).^{18, 19} Furthermore, the absorption band at 3600–3100 cm⁻¹, corresponding to the O–H bond on cellulose, decreased in intensity. These data supported the progress of the silylation reaction of cellulose with the monohydrosilane.

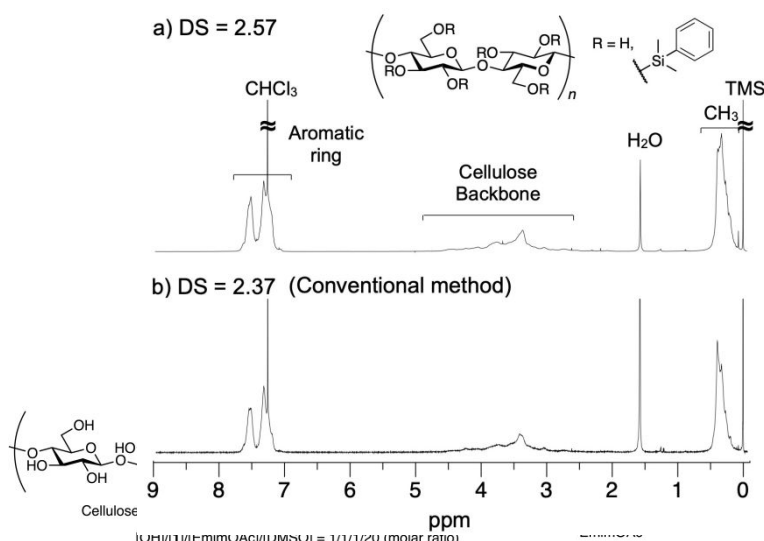
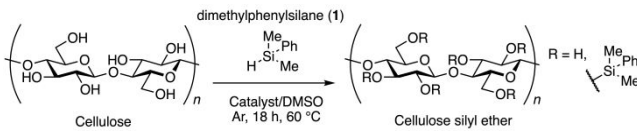
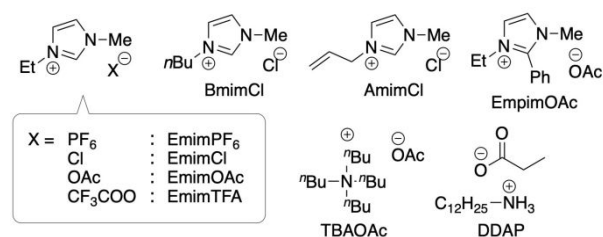


Figure 2. ¹H NMR spectra of the (a) resulting cellulose dimethylphenylsilyl ether (DS = 2.57) in the mixture of EmimOAc/DMSO (1/20 molar ratio) and (b) cellulose prepared by the conventional method in CDCl₃ at 60 °C for 18 h.

Table 1. Effects of ionic compounds on cellulose silylation.^a


Entry	Catalyst	Solution state	DS
1	none	heterogenous	n.d. ^b
2 ^c	none	homogenous	n.d. ^b
3	EmimPF ₆	heterogenous	n.d. ^b
4	EmimCl	heterogenous	n.d. ^b
5	AmimCl	homogenous	n.d. ^b
6	BmimCl	homogenous	n.d. ^b
7	EmimOAc	homogenous	2.57
8	EmimTFA	heterogenous	n.d. ^b
9 ^d	EmimOAc	heterogenous	n.d. ^b
10	EmpimOAc	homogenous	2.00
11	DDAP	heterogenous	n.d. ^b
12	KOAc	heterogenous	n.d. ^b
13	K ₂ CO ₃	heterogenous	n.d. ^b
14	TBAOAc	homogenous	2.24

^aReaction conditions: [ROH]/[1]/[catalyst]/[DMSO] = 1:1:1:20 (molar ratio); 18 h; 60 °C; Ar atmosphere. ^bBased on the absorption band at approximately 1250 cm⁻¹, corresponding to the silyl group in the IR spectrum (Figure S1). ^c7 wt% LiCl containing DMA was used instead of DMSO. ^dTHF was used instead of DMSO.

**Figure 3.** Chemical structures of onium salts.

The ¹H NMR spectrum of the obtained product in CDCl₃ showed peaks at 7.7–6.9 ppm for the aromatic ring of the silyl ether, 5.0–2.7 ppm for the cellulose backbone, and 0.7–0.1 ppm for the two methyl groups on the silyl ether (Figure 2a). Therefore, the synthesis of the desired cellulose dimethylphenylsilyl ether was confirmed. The degree of substitution (DS) of the resulting product was determined by the integral ratio between the peaks for the cellulose backbone and methyl group in the ¹H NMR spectra. As indicated by these ¹H NMR data, the DS value of the desired dimethylphenylsilyl ether group was estimated to be 2.57. This value was higher than that of the polymers (DS = 2.37) synthesized using 1-butyl-3-methylimidazolium chloride (BmimCl), dimethylphenylsilyl chloride, and triethylamine instead of EmimOAc and dimethylphenylsilane (Figure 2b). Size exclusion chromatography (SEC) data of the polymer obtained by the

dehydrogenative silylation method showed that the number average molecular weight (M_n) was 3.5×10^4 with molecular weight distribution (M_w/M_n) of 3.9, and this result was consistent for the natural carbohydrate-based polymer (Table S1).⁴⁴ The cellulose silyl ether was soluble in a wide range of hydrophobic organic solvents based on the results of silylation (Table S2).

As a control experiment, only DMSO was used as the solvent without EmimOAc, and cellulose was not dissolved in the solution (Table 1, Entry 1). As expected, the corresponding IR band (approximately 1250 cm⁻¹), indicating the presence of a silyl ether group, was not observed in the data for the resulting product (Figure S1). In the case of the conventional *N,N*-dimethylacetamide (DMA)/LiCl system, cellulose was homogeneously dissolved in DMA/LiCl solution; however, the recovered polymer did not show an absorption band at 1250 cm⁻¹ in the IR data, probably because of the absence of catalytic activity in this system for the dehydrogenative silylation (Entry 2). When Emim hexafluorophosphate (EmimPF₆) and Emim chloride (EmimCl) were used, the cellulose did not completely dissolve in the solution and the reaction did not proceed (Entries 3 and 4). In contrast, the cellulose was dissolved in 1-allyl-3-methylimidazolium chloride (AmimCl)- and BmimCl-mixed DMSO solution; however, no IR absorption band was derived from the silyl ether group in the recovered polymers, suggesting that ILs play two roles: solvent and catalyst (Entries 5 and 6).

As shown in Table S3, preliminary model experiments using monol (**A**) showed that EmimOAc exhibited catalytic activity for the dehydrogenative silylation of alcohols while generating detectable molecular hydrogen gas (Figure S2), even with a catalytic amount (10 mol%) (Table S3, Entries 4 and 5). In this model experiment, the DMA/LiCl and BmimCl systems did not afford the corresponding silyl ethers (Table S3, Entries 2 and 3, respectively). In the case of Emim trifluoroacetate (EmimTFA) with a less basic carboxylate anion, the cellulose did not dissolve in the solution, and the reaction did not proceed (Table 1, Entry 8). Model experiments showed that EmimTFA had almost no catalytic activity compared to EmimOAc, suggesting that the basicity of the carboxylate anion strongly contributed to its catalytic activity (Table S3, Entry 6). In the case of EmimOAc, the solvent scope was preliminarily investigated; cellulose barely dissolved in THF⁴¹, and in the IR spectrum of the recovered product, the band at approximately 1250 cm⁻¹, derived from the silyl ether group, was almost not observed (Table 1, Entry 9).

Some studies have shown that *N*-heterocyclic carbene (NHC), which is generated by the deprotonation of the C2 proton of the imidazolium salts, can act as a catalyst for dehydrogenative silylation.^{38,45} To confirm the effect of the C2 position, 1-methyl-2-phenyl-3-ethyl imidazolium acetate (EmpimOAc) capped at the C2 position with a phenyl group was prepared and used, followed by the dehydrogenative silylation of cellulose under homogenous conditions, which afforded the desired product with a similar DS value (2.00) to that of EmimOAc (Table 1, Entry 10). This result indicated that the imidazolium-based ILs could undergo dehydrogenative silylation without involving the NHC-

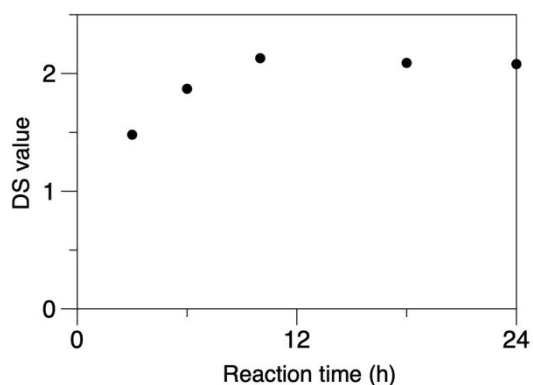


Figure 4. Time-dependent change in the DS value during cellulose phenyldimethylsilyl ether synthesis. Reaction conditions: $[\text{OH}]/[\mathbf{1}]/[\text{EmimOAc}]/[\text{DMSO}] = 1:1:1:20$ (molar ratio); Ar atmosphere at 60 °C.

related reaction mechanism.^{38, 46-48} Corriu's dodecylammonium propionate salt (DDAP)²⁵ was also investigated (Table 1, Entry 11), but the reaction mixture was heterogeneous, and an IR band at approximately 1250 cm^{-1} was barely observed. This result clearly indicated that the IL should act not only as a catalyst for dehydrogenative silylation, but also as a solvent for cellulose. In addition, potassium acetate (KOAc)²⁶ and potassium carbonate (K_2CO_3)⁴⁰ were examined as metal carboxylate salts, and this system afforded similar results as those with DDAP, probably because of the low solubility of cellulose in these systems (Table 1, Entries 12 and 13). Additionally, tetrabutylammonium acetate (TBAOAc), which is known to dissolve cellulose when mixed with DMSO^{43, 49}, underwent the desired silylation with a slightly lower reactivity (DS = 2.24) than that of EmimOAc (Table 1, Entry 14). The effect of cations on the reaction rate was preliminarily demonstrated in model experiments, confirming that quaternary ammonium salts, which exhibited relatively weak interactions with anions, exhibited high catalytic activities (Table S3, Entries 4 and 7–9). These results showed that commercially available EmimOAc was an optimal IL for cellulose dehydrogenative silylation in the IL system and played a dual role as a solvent and catalyst.

Next, the kinetics of the dehydrogenative silylation of cellulose in EmimOAc were investigated. Figure 4 shows the time-dependent change in the DS value of cellulose dimethylphenylsilyl ether using dimethylphenylsilane (**1**) at 60 °C. The plot of time versus DS value reached saturation in EmimOAc in approximately 10 h.

The scope of monohydrosilane is shown in Table 2. Unless otherwise noted, equimolar amounts of hydrosilane were added to the solvent system of EmimOAc/DMSO (1/20, molar ratio) and stirred for 18 h at 60 °C under an Ar atmosphere. Entry 2 shows the effect of the dimethylphenylsilane (**1**) amount; the DS value slightly increases upon using three equivalents of **1** ($[\mathbf{1}]/[\text{ROH}] = 3$). When the reaction was carried out using bulkier and more hydrophobic methyl diphenylsilane (**2**) and triphenylsilane (**3**), the corresponding cellulose silyl ethers with moderate DS values were obtained (Entries 3 and 4).

Table 2. Scope of monohydrosilane for dehydrogenative silylation of cellulose in EmimOAc/DMSO mixed solvent.^a

Entry	Monohydrosilane	Cellulose silyl ether	DS
1		$\text{R}' = \text{Me}$	2.57
2 ^b		$\text{R}' = \text{Me}$	2.69
3		$\text{R}' = \text{Ph}$	2.15
4		$\text{R}' = \text{Ph}$	1.53
5		$\text{R}' = \text{Et}$	trace ^c
6 ^b		$\text{R}' = \text{Et}$	0.32

^aReaction conditions: $[\text{ROH}]/[\text{Monohydrosilane}]/[\text{EmimOAc}]/[\text{DMSO}] = 1:1:1:20$ (molar ratio); 18 h; 60 °C; Ar atmosphere.

^b $[\text{ROH}]/[\text{Monohydrosilane}]/[\text{EmimOAc}]/[\text{DMSO}] = 1:3:1:20$ (molar ratio).

^cBased on the absorption band at approximately 1250 cm^{-1} , corresponding to the silyl group in the IR spectrum (Figure S2)

The slight decrease in the DS value was presumably due to the steric hindrance of the aromatic rings in monohydrosilane. In contrast, when triethylsilane (**4**) was employed as the trialkylsilane, the progress of the reaction with cellulose was barely observed (Entry 5). The possibility of the hydrolysis of cellulose triethylsilyl ether under these reaction conditions was speculated, and the corresponding sample (DS = 2.27) were prepared by conventional silylation using triethylsilylchloride as the silylating reagent (see supporting information). After the stability test of the sample upon heating in the EmimOAc/DMSO solvent mixture, almost no change due to hydrolysis was observed in the ¹H NMR data (Figure S5). It has been reported that the Lewis acidity of the hydrosilanes affects the reactivity of dehydrogenative silylation under basic conditions. The aromatic ring, sp^2 -hybridized substituent, increased the Lewis acidity on the silicon (Si) atom, and increased the reactivities of the monohydroarylsilanes (**1**, **2**, and **3**) compared to the triethylsilane having no aromatic ring (**4**). These tendencies were also observed in similar base-promoted dehydrogenative silylations.³⁰ In the case of using three equivalents of **4** ($[\mathbf{4}]/[\text{ROH}] = 3$), the DS value was estimated to be 0.32 after peracetylation.

Based on a previously reported reaction mechanism,^{30, 31, 50} the predicted reaction mechanism is shown in Figure S6. It was

reported that in DMSO, the acetate anion is more basic than amine⁵¹, capable of catalyzing the dehydrogenative silylation of alcohol⁵⁰, and in basic ionic liquids, such as EmimOAc, the nucleophilicity of the alcohol is enhanced.⁵² After the formation of a more hydridic hydrosilane intermediate (**I**) with the alkoxide coordinated to the Lewis acidic σ -hole on Si with the cooperative assistance of EmimOAc⁴⁴, reaction with a proton source such as acetic acid or alcohol (**II**) produced the desired silyl ether, with the elimination of molecular hydrogen and regeneration of EmimOAc^{30, 50, 53}. Alternatively, intermediates (**I**) and (**II**) may occur simultaneously through a concerted mechanism (**III**), which is often proposed in EmimOAc⁴⁴, to avoid the formation of strongly basic alkoxides; however, a more detailed mechanistic study is required to clarify the entire catalytic system.³⁰

Thus, cellulose silyl ethers could be obtained by mixing cellulose and various monohydrosilanes in ionic liquid under conditions affording high atom economy, releasing only molecular dihydrogen as a formal by-product.

As shown in Table 2, in the reaction using 120 mg of cellulose and 303 mg of dimethylphenylsilane ($[\text{OH}]/[\mathbf{1}] = 1/1$, molar ratio; Entry 1), the amount of the theoretical product of completely substituted cellulose dimethylphenylsilyl ether (DS = 3.0) is 412 mg, and 327 mg of cellulose dimethylphenylsilyl ether (DS = 2.57) is obtained in 79.4% isolated yield. The atom economy of this reaction was very high (98.9%) for cellulose silylation, and the reaction mass efficiency⁵⁴, which is a green chemistry metric, was estimated to be 78.5%.

Highly substituted cellulose silyl ethers were soluble in volatile solvents such as dichloromethane. Figure 5 shows the cast film of cellulose dimethylphenylsilyl ether (DS = 2.57, Table 2, Entry 1) prepared from the dichloromethane solution. The obtained film was transparent, and the sentences printed on the paper through the film could be visually recognized.

Conclusions

In conclusion, a dehydrogenative silylation method for cellulose using monohydrosilane was developed by dissolving cellulose and monohydrosilane in an IL-containing solvent system without any additional catalysts as activators with high atom economy. The ILs used for this reaction system were required to function as the solvents and catalysts, controlled by a combination of cations and anions, with imidazolium cations and carboxylate salts acting as effective ILs. The monohydrosilane bearing an aromatic ring afforded a relatively high degree of substitution for cellulose silyl ether. The atom economy of this reaction system was ca. 99%, and the reaction mass efficiency was estimated to be approximately 79% for dimethylphenylsilane. The investigations to expand the scope of the substrates, application to biomass materials such as other polysaccharides (amylose, chitin, etc.), and research on regioselectivity, catalytic activity, and reaction mechanisms using computational chemistry are currently in progress in our laboratory.



Figure 5. Photograph of cellulose dimethylphenylsilyl ether films (DS = 2.57) obtained via Scheme 2 cast from dichloromethane solution.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

S. B. W. K. are thankful for kind support of Indonesian Endowment Fund for Education (LPDP), Ministry of Finance; and Directorate for Resources, Ministry of Education Culture, Research, and Technology, Republic of Indonesia. This work was predominantly funded by the Japan Science and Technology Agency (JST) (grant number JPMJPF2102) and the Japan Society for the Promotion of Science (JSPS) KAKENHI (grant numbers 18H02253 and 22H02404).

Notes and references

1. A. Gandini, *Macromolecules*, 2008, **41**, 9491-9504.
2. T. Iwata, *Angew. Chem., Int. Ed.*, 2015, **54**, 3210-3215.
3. D. Klemm, B. Heublein, H. P. Fink and A. Bohn, *Angew. Chem., Int. Ed.*, 2005, **44**, 3358-3393.
4. D. Klemm and A. Stein, *J. Macromol. Sci. - Pure Appl. Chem.*, 1995, **A32**, 899-904.
5. J. D. Kittle, C. Wang, C. Qian, Y. Zhang, M. Zhang, M. Roman, J. R. Morris, R. B. Moore and A. R. Esker, *Biomacromolecules*, 2012, **13**, 714-718.
6. F. Z. Khan, T. Sakaguchi, M. Shiotsuki, Y. Nishio and T. Masuda, *Macromolecules*, 2006, **39**, 6025-6030.
7. A. Koschella, T. Heinze and D. Klemm, *Macromol. Biosci.*, 2001, **1**, 49-54.
8. S. C. Fox, B. Li, D. Xu and K. J. Edgar, *Biomacromolecules*, 2011, **12**, 1956-1972.
9. K. Kurita, K. Sugita, N. Kodaira, M. Hirakawa and J. Yang, *Biomacromolecules*, 2005, **6**, 1414-1418.
10. M. Kostag, M. Gericke, T. Heinze and O. A. El Seoud, *Cellulose*, 2019, **26**, 139-184.
11. K. N. Onwukamike, S. Grelier, E. Grau, H. Cramail and M. A. R. Meier, *ACS Sustain. Chem. Eng.*, 2019, **7**, 1826-1840.
12. T. Welton, *Chem. Rev.*, 1999, **99**, 2071-2084.
13. R. P. Swatloski, S. K. Spear, J. D. Holbrey and R. D. Rogers, *J. Am. Chem. Soc.*, 2002, **124**, 4974-4975.
14. C. Li, B. Knierim, C. Manisseri, R. Arora, H. V. Scheller, M. Auer, K. P. Vogel, B. A. Simmons and S. Singh, *Bioresour. Technol.*, 2010, **101**, 4900-4906.

15. H. Ohno and Y. Fukaya, *Chem. Lett.*, 2009, **38**, 2-7.
16. M. Pei, X. W. Peng, Y. Q. Shen, Y. L. Yang, Y. L. Guo, Q. Zheng, H. B. Xie and H. Sun, *Green Chem.*, 2020, **22**, 707-717.
17. R. Milotskyi, G. Sharma, T. Fujie, D. Hirose, N. Wada and K. Takahashi, *React. Chem. Eng.*, 2023, **8**, 1395-1402.
18. S. Kohler, T. Liebert and T. Heinze, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 4070-4080.
19. W. Mormann and M. Wezstein, *Macromol. Biosci.*, 2009, **9**, 369-375.
20. K. Petzold, A. Koschella, D. Klemm and B. Heublein, *Cellulose*, 2003, **10**, 251-269.
21. B. M. Trost, *Science*, 1991, **254**, 1471-1477.
22. S. Kim, M. S. Kwon and J. Park, *Tetrahedron Lett.*, 2010, **51**, 4573-4575.
23. J. M. S. Cardoso, R. Lopes and B. Royo, *J. Organomet. Chem.*, 2015, **775**, 173-177.
24. H. Li, H. Guo, Z. Li, C. Wu, J. Li, C. Zhao, S. Guo, Y. Ding, W. He and Y. Li, *Chem. Sci.*, 2018, **9**, 4808-4813.
25. J. Boyer, R. J. P. Corriu, R. Perz and C. Reye, *J. Organomet. Chem.*, 1978, **145**, C31-C33.
26. J. Boyer, R. J. P. Corriu, R. Perz and C. Reye, *J. Organomet. Chem.*, 1978, **157**, 153-162.
27. J. Boyer, R. J. P. Corriu, R. Perz and C. Reye, *J. Organomet. Chem.*, 1978, **148**, C1-C4.
28. F. Le Bideau, J. Hénique, E. Samuel and T. Coradin, *Chem. Commun.*, 2001, **15**, 1408-1409.
29. M. J. Zacuto, S. J. O'Malley and J. L. Leighton, *J. Am. Chem. Soc.*, 2002, **124**, 7890-7891.
30. A. Weickgenannt and M. Oestreich, *Chem. Asian J.*, 2009, **4**, 406-410.
31. A. A. Toutov, K. N. Betz, M. C. Haibach, A. M. Romine and R. H. Grubbs, *Org. Lett.*, 2016, **18**, 5776-5779.
32. A. Harinath, J. Bhattacharjee, S. Anga and T. K. Panda, *Aust. J. Chem.*, 2017, **70**, 724-730.
33. L. Horner and J. Mathias, *J. Organomet. Chem.*, 1985, **282**, 155-174.
34. Y. Tanabe, H. Okumura, A. Maeda and M. Murakami, *Tetrahedron Lett.*, 1994, **35**, 8413-8414.
35. J. M. Blackwell, K. L. Foster, V. H. Beck and W. E. Piers, *J. Org. Chem.*, 1999, **64**, 4887-4892.
36. M. Ueno, M. Yonemoto, M. Hashimoto, A. E. Wheatley, H. Naka and Y. Kondo, *Chem. Commun.*, 2007, **22**, 2264-2266.
37. A. Grajewska and M. Oestreich, *Synlett*, 2010, **16**, 2482-2484.
38. D. Gao and C. Cui, *Chem. Eur. J.*, 2013, **19**, 11143-11147.
39. U. Kaya, U. P. Tran, D. Enders, J. Ho and T. V. Nguyen, *Org. Lett.*, 2017, **19**, 1398-1401.
40. N. A. DeLucia, N. Das and A. K. Vannucci, *Org. Biomol. Chem.*, 2018, **16**, 3415-3418.
41. M. Gericke, T. Liebert, O. A. El Seoud and T. Heinze, *Macromol. Mater. Eng.*, 2011, **296**, 483-493.
42. J. M. Andanson, E. Bordes, J. Devemy, F. Leroux, A. A. H. Padua and M. F. C. Gomes, *Green Chem.*, 2014, **16**, 2528-2538.
43. A. Idstrom, L. Gentile, M. Gubitosi, C. Olsson, B. Stenqvist, M. Lund, K. E. Bergquist, U. Olsson, T. Kohnke and E. Bialik, *Cellulose*, 2017, **24**, 3645-3657.
44. R. Kakuchi, R. Ito, S. Nomura, H. Abroshan, K. Ninomiya, T. Ikai, K. Maeda, H. J. Kim and K. Takahashi, *RSC Adv.*, 2017, **7**, 9423-9430.
45. D. Gatineau, Q. Zhao, D. P. Curran, M. Malacria, E. Lacote, L. Fensterbank and J. P. Goddard, *Dalton Trans.*, 2013, **42**, 7458-7462.
46. D. Hirose, S. B. W. Kusuma, D. Ina, N. Wada and K. Takahashi, *Green Chem.*, 2019, **21**, 4927-4931.
47. S. B. W. Kusuma, D. Hirose, A. Yoshizawa, L. Szabó, D. Ina, N. Wada and K. Takahashi, *ACS Sustain. Chem. Eng.*, 2021, **9**, 8450-8457.
48. A. Yoshizawa, C. Maruyama, S. B. Kusuma, N. Wada, K. Kuroda, D. Hirose and K. Takahashi, *Polymers*, 2023, **15**, 419.
49. J. J. Miao, H. B. Sun, Y. Q. Yu, X. L. Song and L. P. Zhang, *RSC Adv.*, 2014, **4**, 36721-36724.
50. E. D. Voronova, I. E. Golub, A. Pavlov, N. V. Belkova, O. A. Filippov, L. M. Epstein and E. S. Shubina, *Inorg. Chem.*, 2020, **59**, 12240-12251.
51. S. T. Heller and T. P. Silverstein, *ChemTexts*, 2020, **6**, 15.
52. W. R. Fawcett, P. Brooksby, D. Verbovy, L. Bako and G. Palinkas, *J. Mol. Liq.*, 2005, **118**, 171-178.
53. D. D. Xu, J. C. Chen, J. Y. Li, Y. B. Zhu, S. Y. Wu, J. Q. Zhang, X. Y. Liu and B. M. Fan, *Asian J. Org. Chem.*, 2021, **10**, 1402-1405.
54. D. J. C. Constable, A. D. Curzons and V. L. Cunningham, *Green Chem.*, 2002, **4**, 521-527.