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AB₂ polymerization on hollow microporous organic polymers: engineering of solid acid catalysts for the synthesis of soluble cellulose derivatives[†]

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This work shows a new post-synthetic strategy of a microporous organic polymer (MOP) based on AB₂ polymerization chemistry (polymerization of AB₂-type monomers). Hollow MOP (H-MOP) platforms were prepared by template synthesis *via* Sonogashira coupling of 1,4-dibromo-2,5-diethynylbenzene. The amount of terminal alkynes in the H-MOP was amplified *via* AB₂ polymerization. Through the thiol-yne click reaction, aliphatic sulfonic acids were incorporated into the terminal alkyne-enriched H-MOP. The resultant solid acid catalysts showed efficient performance in the synthesis of soluble cellulose derivatives.

Post-synthetic modification (PSM) is a powerful strategy for incorporating tailored functionality into microporous organic polymers (MOPs).¹ Compared to the pre-designed building block strategy,² relatively simple building blocks can be used for the synthesis of MOP platforms.³ There have been recent reports on the PSM of MOPs.^{3,4} In these reports, functional groups in MOPs could be further modified *via* simple organic reactions.^{3,4}

AB₂-type monomers show a unique feature in the formation of polymeric structures.⁵ A chemical reaction of A and B between AB₂-type monomers results in highly branched materials.⁵ Moreover, it can be speculated that the PSM of MOPs based on the AB₂ polymerization may result in enrichment of B. For example, if A and B are an azide group and a terminal alkyne group, respectively, the AB₂-type monomers can be polymerized *via* the azide–alkyne click reaction,⁶ resulting in highly branched materials with enriched terminal alkynes (Fig. 1a and b).

^aDepartment of Chemistry, Sungkyunkwan University, Suwon 16419, Korea. E-mail: sson@skku.edu Recently, it has been reported that thiols can be added to alkynes in MOPs *via* the thiol–yne click reaction.^{3b} Moreover, we observed that terminal alkynes are much more reactive toward thiol addition than internal alkynes⁷ (Fig. 1c). Amorphous MOP materials prepared by Sonogashira coupling have intrinsic connection defects, resulting in a minor amount of terminal alkynes in the materials. If the amount of terminal alkyne-rich MOP can be a good platform for the engineering of functional materials through alkyne-related PSM.

Recently, there have been increasing reports on the utilization of plants as sustainable chemical resources, instead of depletable petroleum.⁸ Cellular walls of plants consist of cellulose, hemicelluloses, and lignins.⁸ Cellulose can be utilized for the engineering of functional films, membranes, and fibers.⁹ However, cellulose has a multiple hydrogen bonding network and poor solubility in most solvents, making engineering of cellulose hard. Thus, chemical transformations to soluble cellulose derivatives have attracted significant atten-



Fig. 1 (a) Azide-alkyne click reaction, (b) polymerization of AB_2 -type monomers by the azide-alkyne click reaction to enrich terminal alkynes, and (c) thiol-yne click reaction.

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tion from scientists.¹⁰ The hydrogen bonding network of cellulose can be hindered through the protection of its hydroxy groups. For example, acetylation of cellulose can be an efficient way to generate a soluble cellulose derivative, cellulose acetate.¹⁰ For this, solid acid catalysts such as commercial Amberlyst-15 (75–300 wt% of cellulose) have been used.¹⁰ However, more studies are needed to develop more efficient solid acid catalysts.

Recently, our research group has developed new solid acid catalysts based on MOP chemistry.⁷ Terminal alkynes could be utilized for the introduction of aliphatic sulfonic acids (AS) through the thiol-yne click reaction. However, because the terminal alkynes originate from structural defects of networking, the content of terminal alkynes is minor in MOPs. In this work, we report that the content of terminal alkynes can be amplified *via* AB₂ polymerization on hollow MOP (H-MOP) platforms. The terminal alkyne-enriched MOP was used as a platform for the engineering of an AS-enriched solid acid catalyst, showing efficient catalytic performance in the synthesis of soluble cellulose acetate.

Fig. 2 shows synthetic schemes of the H-MOP with aliphatic sulfonic acids (H-MOP-AS) and the AS-enriched H-MOP *via* AB₂ polymerization (H-MOP@AB₂-AS).



The H-MOP bearing terminal alkynes (H-MOP-TA) was prepared by Sonogashira coupling of 1,4-dibromo-2,5-diethynylbenzene in the presence of silica spheres and by successive silica etching.⁷ To enhance the contents of terminal alkynes, the H-MOP-TA was reacted with an AB₂-type monomer, 3,5diethynylbenzyl azide, through the azide–alkyne click reaction, resulting in a terminal alkyne-enriched H-MOP (H-MOP@AB₂-TA). Through the thiol–yne click reaction of H-MOP-TA and H-MOP@AB₂-TA with sodium 3-mercapto-1-propanesulfonate and successive acid quenching, H-MOP-AS (a control material) and H-MOP@AB₂-AS were prepared (Fig. 2 and refer to experimental procedures in the ESI†).

The PSM process of H-MOP-TA by the AB_2 polymerization was characterized by various analysis methods (Fig. 3). Scanning (SEM) and transmission electron microscopy (TEM) showed that the H-MOP-TA has a hollow structure with an average dia-



Fig. 2 Synthetic schemes for the hollow MOP with aliphatic sulfonic acids (H-MOP-AS) and AS-enriched H-MOP via AB_2 polymerization (H-MOP@AB₂-AS).

Synthetic Modification

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H-MOP@AB2-AS

Fig. 3 SEM and TEM images of H-MOP-TA (a and b), H-MOP@AB₂-TA-0.5 (c and d), H-MOP@AB₂-TA-1 (e and f), and H-MOP@AB₂-TA-2 (g and h). (i) N₂ sorption isotherm curves at 77 K and pore size distribution diagrams (based on the DFT method) of H-MOP-TA and H-MOP@AB₂-TA-2. (j) IR spectra, and (k) solid state ¹³C NMR spectra of H-MOP-TA, H-MOP@AB₂-TA-0.5, H-MOP@AB₂-TA-1, and H-MOP@AB₂-TA-2.

H-MOP@AB2-TA

meter and a shell thickness of 268 and 23 nm, respectively (Fig. 3a and b). In the synthesis of H-MOP@AB₂-TA, we systematically increased the amount of the AB₂ monomer from 0.18 mmol to 0.36 and 0.72 mmol, resulting in H-MOP@AB₂-TA-0.5, H-MOP@AB₂-TA-1, and H-MOP@AB₂-TA-2, respectively. As the amount of the AB₂ monomer increased, the shell thickness of H-MOP@AB₂-TA gradually increased from 26 nm (H-MOP@AB₂-TA-0.5) to 31 nm (H-MOP@AB₂-TA-1) and 37 nm (H-MOP@AB₂-TA-2) (Fig. 3c-h). When we increased the amount of the AB₂ monomer to 1.44 mmol, the resultant H-MOP@AB₂-TA-4 was mixed with additional irregular polymeric materials, due to separate formation of AB₂ polymers (Fig. S1 in the ESI†).

According to the analysis of Type I N₂ sorption isotherm curves, the surface area and the micropore volume of H-MOP-TA were found to be 522 m² g⁻¹ and 0.14 cm³ g⁻¹, respectively (Fig. 3i). The surface area and the micropore volume of H-MOP@AB₂-TA-2 decreased to 277 m² g⁻¹ and 0.07 cm³ g⁻¹, respectively, due to nonporous nature of AB₂ polymers (Fig. 3i). In the infrared (IR) absorption spectrum of H-MOP-TA, the vibration peak of terminal alkynes was observed at 3300 cm⁻¹ (Fig. 3j). In cases of H-MOP@AB₂-TA-0.5, H-MOP@AB₂-TA-1, and H-MOP@AB₂-TA-2, the intensities of terminal alkyne peaks gradually increased with an increasing amount of the AB₂ polymer.

Solid state ¹³C nuclear magnetic resonance spectroscopy (NMR) of H-MOP-TA showed ¹³C peaks at 124–134, 93, and 80 ppm, corresponding to aromatic groups, internal alkynes, and terminal alkynes, respectively (Fig. 3k). In ¹³C spectra of H-MOP@AB₂-TA materials, new ¹³C peaks appeared at 146 and 52 ppm, corresponding to triazole rings and benzyl carbons of the AB₂ polymer, respectively. In addition, the intensities of ¹³C peaks of terminal alkynes (at 80 ppm) increased, compared to that of H-MOP-TA, confirming the successful incorporation of AB₂ polymers into H-MOP-TA. According to elemental analysis, nitrogen contents increased gradually from 4.32 wt% (MOP@AB₂-TA-0.5) to 7.24 wt% (MOP@AB₂-TA-1) and 10.00 wt% (MOP@AB₂-TA-2), corresponding to 1.02, 1.72, and 2.38 mmol AB₂ monomers per g, respectively.

Considering the existence of terminal alkynes in H-MOP-TA and H-MOP@AB2-TA-2, we introduced aliphatic sulfonic groups into the materials using sodium 3-mercapto-1-propanesulfonate through thiol-yne click reactions followed by acid quenching. SEM and TEM images of the resultant H-MOP-AS and H-MOP@AB2-AS showed the complete retention of original hollow structures with shell thicknesses of 23 and 37 nm, respectively (Fig. 4a-d). Type I N₂ sorption isotherm curves of the H-MOP-AS and H-MOP@AB2-TA-2 indicated the microporosity of materials (Fig. 4e and f). Through the PSM of H-MOP-TA to H-MOP-AS, surface areas decreased from 522 m² g^{-1} to 384 m² g⁻¹, matching well with the conventional observations in the PSM of MOP materials reported in the literature.3,4,7 Interestingly, in the case of the PSM of H-MOP@AB₂-TA-2, the change of the surface area was relatively insignificant with a decrease from 277 m² g⁻¹ to 200 m² g⁻¹



Fig. 4 SEM and TEM images of (a and b) H-MOP-AS and (c and d) H-MOP@AB₂-AS. (e and f) N₂ adsorption-desorption isotherm curves and pore size distribution diagrams (based on the DFT method), (g and h) IR absorption spectra, and (i) solid state ¹³C NMR spectra of H-MOP-TA, H-MOP-AS, H-MOP@AB₂-TA-2, and H-MOP@AB₂-AS.

(H-MOP@AB₂-AS), which is attributable to the PSM of nonporous AB₂ polymers.

IR absorption spectra of H-MOP-AS and H-MOP@AB₂-AS showed new peaks at 3438, 1631, and 1218 cm⁻¹, corresponding to O–H, C=C, and S=O vibrations, respectively, indicating that aliphatic sulfonic acids were incorporated through the thiol-yne click reaction⁷ (Fig. 4g and h). Solid state ¹³C NMR spectra of H-MOP-AS and H-MOP@AB₂-AS showed disappearance of terminal alkyne peaks at 80 ppm and appearance of new ¹³C peaks at 49 and 17–35 ppm, corresponding to the propylene moieties of aliphatic sulfonic acid groups

(Fig. 4i). According to elemental analysis, sulfur contents of H-MOP-AS and H-MOP@AB₂-AS were found to be 3.39 and 8.28 wt%, corresponding to 0.53 and 1.29 mmol sulfonic acids per g, respectively. Powder X-ray diffraction studies showed that all MOP materials in this work are amorphous, which is a conventional feature of MOP materials prepared by Sonogashira coupling in the literature¹¹ (Fig. S2 in the ESI†). Thermogravimetric analysis showed that the H-MOP-AS and H-MOP@AB₂-AS are thermally stable up to 225 and 201 °C, respectively (Fig. S3 in the ESI†).

Considering the solid acidic feature of H-MOP($@AB_2$ -AS, we studied its catalytic performance in the synthesis of soluble cellulose acetate from cellulose, compared to H-MOP-AS and commercial Amberlyst-15. Fig. 5 and S4 in the ESI,† and Table 1 summarize the results.



Fig. 5 (a) Synthetic scheme of cellulose acetate from cellulose and photographs of cellulose and cellulose acetate (powder form and solutions of 0.15 g/15 mL CH₂Cl₂). (b) Isolated yields and (c) degree of substitution (DS, degree of acetylation per glucose unit) of cellulose acetates obtained from cellulose (0.30 g) using H-MOP-AS, H-MOP@AB₂-AS, and Amberlyst-15 after 10 h at 45 °C (bath temperature) under N₂. (d and e) Recyclability of H-MOP@AB₂-AS in the synthesis of cellulose acetate from cellulose.

It has been reported that optimal reaction conditions of acetylation are important to obtain the cellulose acetate.¹⁰ If cellulose is treated with excessive solid acids, it can be decomposed to black carbon materials through dehydration.¹⁰ In this regard, we investigated the optimal amount of solid acid catalysts with a fixed amount of cellulose in a fixed reaction time (Table 1 and Fig. 5b and c). As shown in Fig. 5b, the maximum isolated yields of cellulose acetate were obtained to be 73, 70, and 70% by the optimized 10, 27, and 100 wt% (to cellulose) of H-MOP@AB₂-AS, H-MOP-AS, and Amberlyst-15, respectively. For the obtained cellulose acetates, degrees of substitution (DS, a degree of acetylation per glucose unit) were found to be 2.78, 2.70, and 2.72 for H-MOP@AB₂-AS, H-MOP-AS, and Amberlyst-15, respectively (Fig. 5c).

While cellulose was completely insoluble in most solvents including methylene chloride, the obtained cellulose acetate by H-MOP@AB₂-AS was very soluble in methylene chloride (Fig. 5a). When excessive solid acid catalysts were used, the DS and isolated yields sharply decreased. Considering the optimal amount of solid acid catalysts, the catalytic efficiency of H-MOP@AB₂-AS is higher than that of H-MOP-AS, and

 Table 1
 Catalytic performance of solid acid catalysts in the synthesis of cellulose acetate from cellulose^a

Entry	Catalysts	Catalyst amount (mg)	Isolated yield (%)	DS^b
1	Amberlyst-15	15		_
2	Amberlyst-15	30	14	2.17
3	Amberlyst-15	45	21	2.35
1	Amberlyst-15	90	26	2.39
5	Amberlyst-15	130	43	2.46
5	Amberlyst-15	160	44	2.48
7	Amberlyst-15	225	63	2.54
3	Amberlyst-15	300	70	2.72
Ð	Amberlyst-15	400	59	2.58
10	Amberlyst-15	450	22	2.50
11	H-MOP-AS	15	19	2.33
12	H-MOP-AS	30	25	2.45
13	H-MOP-AS	45	36	2.51
14	H-MOP-AS	60	56	2.58
15	H-MOP-AS	80	70	2.70
16	H-MOP-AS	90	63	2.61
17	H-MOP-AS	130	15	1.97
18	H-MOP-AS	225	—	_
19	H-MOP@AB2-AS	15	21	2.24
20	H-MOP@AB2-AS	20	28	2.46
21	H-MOP@AB2-AS	25	50	2.54
22	H-MOP@AB2-AS	30	73	2.78
23	H-MOP@AB2-AS	35	58	2.68
24	H-MOP@AB2-AS	40	42	2.66
25	H-MOP@AB2-AS	45	35	2.61
26	H-MOP@AB2-AS	90	31	2.39
27	H-MOP@AB2-ASc	30	70	2.76
28	H-MOP@AB2-ASd	30	71	2.75
29	H-MOP@AB2-ASe	30	67	2.73
30	H-MOP@AB ₂ -AS ^f	30	68	2.75

^{*a*} Reaction conditions: Cellulose (0.30 g), catalyst, acetic anhydride (0.69 mL, 7.3 mmol), acetic acid (0.78 μ L, 14 μ mol), CH₂Cl₂ (6 mL), 45 °C (bath temperature), 10 h, N₂. ^{*b*} Degree of substitution (acetylation per glucose unit) determined by NMR. ^{*c*} The catalyst recovered from entry 22 was used. ^{*d*} The catalyst recovered from entry 27 was used. ^{*e*} The catalyst recovered from entry 28 was used. ^{*f*} The catalyst recovered from entry 29 was used.

Amberlyst-15 by 2.7 and 10 times, respectively, which is attributable to the enriched sulfonic acid groups and the nanostructure of H-MOP@AB₂-AS. Moreover, while H-MOP@AB₂-AS (10 wt% of cellulose) resulted in 73% yield of cellulose acetate, recently, solid acid catalysts (75–300 wt% of cellulose) were used to obtain 21–77% yields of cellulose acetate in the literature.^{10a,d}

Considering the thermal stability of H-MOP@AB₂-AS, we tested its recyclability. In the successive recyclability tests, the H-MOP@AB₂-AS showed isolated yields of 73, 70, 71, 67, and 68% in the first, second, third, fourth, and fifth reactions for the synthesis of cellulose acetate, respectively, maintaining DS values in the range of 2.73–2.78 (Fig. 5d and e and Table 1). SEM and IR studies on the recovered H-MOP@AB₂-AS after five successive runs indicated that the original hollow structure and the chemical structure were retained (Fig. S5 in the ESI[†]).

In conclusion, this work shows new PSM of H-MOP platforms based on AB₂ polymerization. Amplified terminal alkyne groups were further utilized for the engineering of solid acid catalysts bearing aliphatic sulfonic acids. The resultant H-MOP@AB₂-AS showed enhanced catalytic efficiency in the synthesis of cellulose acetate, compared to H-MOP-AS and commercial Amberlyst-15. We believe that the PSM based on AB₂ polymerization on the H-MOP platforms can be further extended to introduce various tailored functionalities.

Conflicts of interest

There are no conflicts to declare.

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