2017～2019年度 関西大学研究拠点形成支援経費研究成果報告書

著者	工藤 宏人, 宮前 翼, 上田 正人, 村山 憲弘, 林 順一, 松岡 光昭, 横山 佳帆, 大倉 滉平, 内藤 牧男, 下山 大輔, 関谷 亮, 灰野 岳晴, 池田 勝彦, 森 重雄, 土井 研児, 北垣 壽, 寺内 俊太郎, 五十井 浩平, 白杉 文香, 丸山 徹, Tamaki Mitsuyoshi, Nakamura Keisuke, Nakamura Gou, 齋藤 隆太, 仲村 利樹, 柳谷 仁志, Sakai Takahiro, 中本 光二, 山口 莉嘉, 藤田 智香, 福永 真理, 塩月 康平, 竹田 紘也, 山本 洋揮, 古澤 孝弘, 渡邊 健夫, 大隈 修, 前 一廣, 鈴木 一誓, 柿沼 綾子, 小俣 孝久, 坂本 貴則, 今坂 怜史, 石井 甫泰, 荒木 貞夫, 山本 秀樹, 大堀 静也, 小川 大貴, Kitagawa Kouta, 関 あずさ, Sonoc Alexandru, Jeswiet Jacob, 芝田 隼次
発行年	2020
権利	2-1 ネットワークポリマー事務局の許諾を得て公開しています。 2-4 日本金属学会の許諾を得て公開しています。 2-6 This is a post-peer-review, pre-copyedit version of an article published in International Journal of Metalcasting. The final authenticated version is available online at http://dx.doi.org/10.1007/s40962-019-00310-7. 2-7 This is a post-peer-review, pre-copyedit version of an article published in International Journal of Metalcasting. The final authenticated version is available online at: http://dx.doi.org/10.1007/s40962-018-00292-y. 2-13 This is the accepted version of the article, which has been published in final form at DOI 10.1016/j.micromeso.2018.07.005. 2-14 (C)フォトポリマー学会　この資料は著者最終...

Synthesis and Metal-Complexation Ability of Cross-Linking Materials Containing Noria-Templated Cavities with Pendant Carboxylic Acid Groups

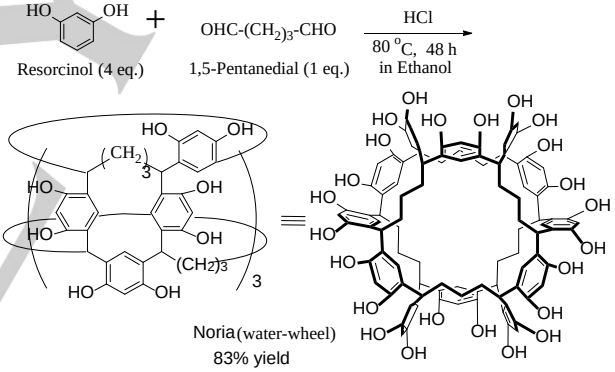
Hiroto Kudo* [a], Tsubasa Miyamae[a], Kouta Kitagawa[a], Kohei Isoi[b], Norihiro Murayama[b], and Jun'ichi Hayashi[b]

Abstract: We synthesized noria-containing cross-linking materials, Cross(Noria-MA-*co*-DM[n]$_m$), by radical polymerization of a noria derivative with pendant methacryloyl groups (noria-MA) and α, ω-alkanedimethacrylamides (DM[n], n = 3, 6, 12) at feed ratios of noria-MA/DM[n] = 1/2.4, 1/12, and 1/24 (m = 2.4, 12. and 24). Alkaline hydrolysis reaction of Cross(Noria-MA-*co*-DM[n]$_m$) removed the noria moieties to give corresponding cross-linking materials, Cross-COOH-DM[n]$_m$, containing noria-templated fixed cavities with pendant carboxylic acid groups. Among the noria-containing cross-linking materials, Cross(Noria-MA-*co*-DM[6]$_{24}$) showed the greatest extent of removal of noria upon hydrolysis. Nitrogen and carbon dioxide absorption studies indicated that Cross(Noria-MA-*co*-DM[6]$_{24}$) contains fixed cavities, whereas Cross-COOH-DM[6]$_{24}$ does not in the solid (unswollen) state. Examination of the inclusion-complex-forming ability of the synthesized cross-linking materials using aqueous solutions of metal ions revealed that Cross-COOH-DM[6]$_{24}$ has the greatest absorption capacity. These results indicate that Cross-COOH-DM[6]$_{24}$ indeed contains noria-templated cavities that can accommodate metal ions in aqueous solution.

Introduction

Crown ethers are well-known macrocycles that form complexes with alkali metal salts, ammonium salts, and many transition metal and lanthanide salts [1 - 3]. However, although crown ethers can accommodate a variety of guest compounds, their selectivity is often poor due to their molecular flexibility. In contrast, cryptands[4 - 6] and spherands[7 – 9], which have three-dimensional cyclic structures, show greater selectivity. Calixarenes containing cone-shape structures with fixed cavities also show complex-forming abilities with metal ions and some organic compounds[10]. Furthermore, cavitands and carserands, which contain intramolecular bridge-units in calixarene-type structures, provide extended cavities, which can accommodate various metal ions and some gases, such as oxygen and carbon disulfide.[11 - 12] In addition, cyclodextrins, which are natural macrocycles containing 1,4-glucose units,[13] have a hydrophilic exterior and a hydrophobic interior, and form complexes selectively with organic compounds in water[14]. Polyrotaxanes[15-17] and nanotubes[18] also have the ability to form complexes with organic compounds.

On the other hand, we synthesized a ladder-type cyclic oligomer, which we called noria (water-wheel in Latin), by means of one-pot reaction using resorcinol and 1,5-pentanedial in high yield.[19] Single-crystal X-ray analysis confirmed that noria has 24 hydroxyl groups, 6 cavities in the side, and a large hydrophobic central hole, i.e., a water-wheel-like structure (Scheme 1). A noria derivative (noria-COOEt) containing carboxylic ester moieties could form a complex with Rb^+ ion, which was apparently enclosed in the central hole in the molecule. Other noria derivatives[20 - 27] and noria-like macrocycle compounds [28 - 31] have since been synthesized and their applications have been investigated.



Scheme 1. Synthesis of Noria

In the present work, we used the noria structure to design and synthesize a new class of cross-linking materials containing noria-templated fixed cavities with pendant carboxylic acid groups, anticipating that they would show distinctive complexation abilities with metal ions. The cross-linking materials were synthesized by radical polymerization of a noria derivative having pendant methacryloyl groups with dimethacrylamides as cross-linkers, followed by aqueous alkaline hydrolysis reaction to remove the noria structures, yielding the corresponding cross-linking materials with noria-templated cavities containing pendant carboxylic acid groups. The adsorption properties of these cross-linking materials for gases (nitrogen and carbon dioxide) in the solid state and the inclusion complex-forming abilities with metal salts in aqueous solution were examined.

Results and Discussion

Synthesis of noria derivative (Noria-MA) with pendant methacryloyl groups

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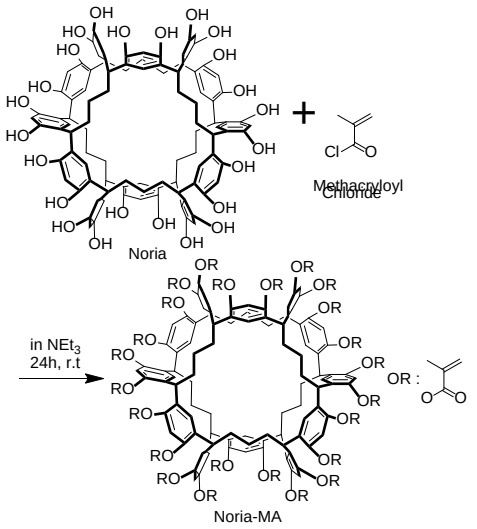
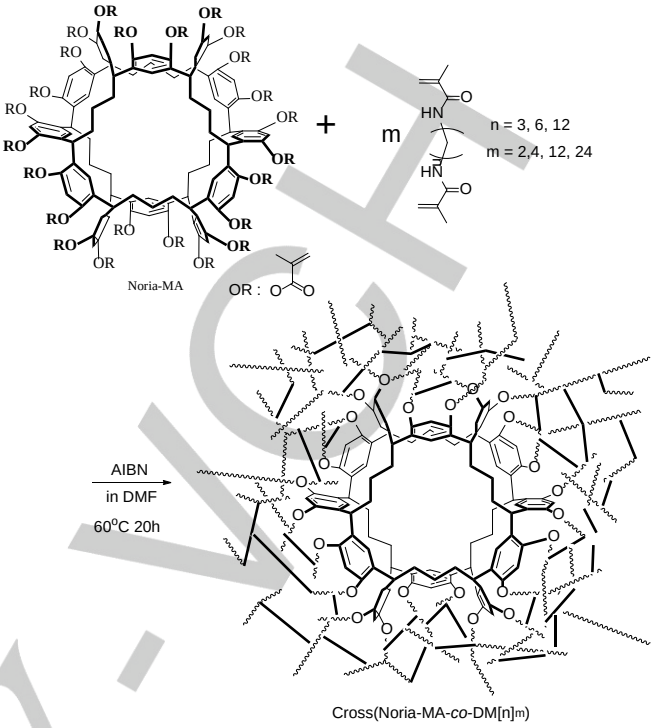
Reaction of noria and methacryloyl chloride was carried out in NEt_3 as a solvent to give the corresponding noria derivative with pendant methacryloyl groups (noria-MA). The structure was confirmed by ^1H NMR and IR spectroscopy. The ^1H NMR spectrum showed peaks at 5.55 ~ 6.18 ppm assignable to methacryloyl groups. The IR spectrum also showed a peak at 1739 cm^{-1} assignable to stretching vibration of carbonyl groups. No peaks assignable to hydroxyl groups were seen in the ^1H NMR and IR spectra. These results indicate that all the hydroxyl groups of noria were converted to methacryloyl groups, i.e., noria-MA was obtained in 20 % yield as shown in Scheme 2.



Scheme 2. Synthesis of Noria-MA.

Radical copolymerization of noria-MA and α,ω-alkanedimethacrylamides (DM[n]) [Synthesis of Cross(Noria-MA-*co*-DM[n]$_m$)].

We examined the synthesis of cross-linking materials by radical copolymerization of noria-MA and α,ω-alkanedimethacrylamides (DM[n], n = 3, 6, 12) (Scheme 3). In the case of 1,6-bis(methacrylamido)hexane (DM[6]), Cross(Noria-MA-*co*-DM[6]$_m$) was obtained in quantitative yield at feed ratios of noria-MA / DM[6] = 1 / 2.4, 1 / 12, and 1 / 24 (m = 2.4, 12, and 24) (Runs 4 ~ 6 in Table 1). Cross(Noria-MA-*co*-DM[3]$_m$) and Cross(Noria-MA-*co*-DM[12]$_m$) were similarly obtained by radical polymerization of noria-MA with DM[3] and DM[12], respectively. The conditions and results are summarized in Table 1.



Scheme 3. Radical polymerization of noria-MA and dimethacrylamides (DM[n]) (n = 3, 6, and 12).

Table 1. Radical copolymerization of noria-MA and DM[n](n = 3, 6, 12)[a]

Run	Feed Ratios Noria-MA/DM[n]	Cross(Noria-MA-*co*-DM[n]$_m$)	Yield (%)	T_d^{i}[b] (°C)
1	Noria-MA/DM[3] = 1.0/2.4	n = 3, m = 2.4	>99	282.1
2	Noria-MA/DM[3] = 1.0/12	n = 3, m =12	>99	280.1
3	Noria-MA/DM[3] = 1.0/24	n = 3, m = 24	>99	282.1
4	Noria-MA/DM[6] = 1.0/2.4	n = 6, m = 2.4	>99	277.5
5	Noria-MA/DM[6] = 1.0/12	n = 6, m =12	>99	277.8
6	Noria-MA/DM[6] = 1.0/24	n = 6, m = 24	>99	277.2
7	Noria-MA/DM[12] = 1.0/2.4	n = 12, m = 2.4	>99	324.5
8	Noria-MA/DM[12] = 1.0/12	n = 12, m =12	>99	324.3
9	Noria-MA/DM[12] = 1.0/24	n = 12, m = 24	>99	325.1

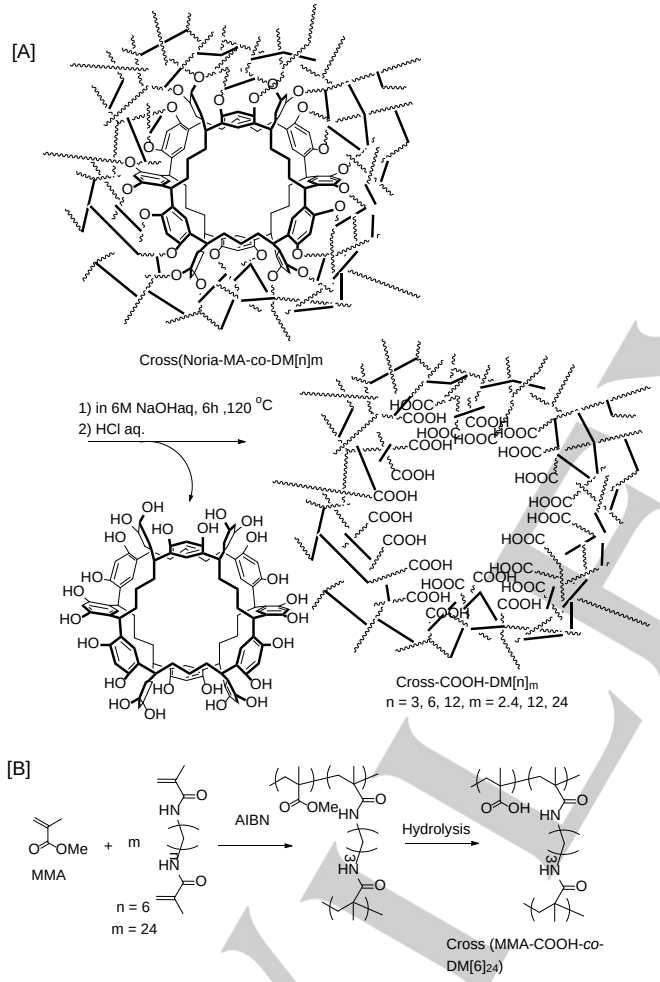
[a] Conditions; AIBN(3 mol%) in DMF at 60 °C for 20 h. [b] Determined by TGA.

Glass transition temperature (T_g) and thermal decomposition temperature (T_d^{i}) were determined by means of DSC and TGA, respectively. No T_g was observed in the range between 25 and 250 °C, and T_d^{i} values were in the range between 277.5 and

325.1 °C. The thermal stability of Cross(Noria-MA-*co*-DM[n]$_m$) was consistent with the structures of the cross-linkers DM[n]. The order of T_d was Cross(Noria-MA-*co*-DM[12]$_m$) > Cross(Noria-MA-*co*-DM[3]$_m$) > Cross(Noria-MA-*co*-DM[6]$_m$).

Hydrolysis of Cross(Noria-MA-*co*-DM[n]$_m$) [Synthesis of Cross-COOH-DM[n]$_m$] (n = 3, 6, 12, m = 2.4, 12, 24)

Hydrolysis reaction was performed in aqueous alkaline solution to remove noria from Cross(Noria-MA-*co*-DM[n]$_m$) (n = 3, 6, 12, m = 2.4, 12, 24) with the aim of obtaining insoluble cross-linking materials with noria-templated fixed holes, as shown in Scheme 4[A], as new functional materials for host-guest chemistry.



Scheme 4. Hydrolysis reaction of Cross(Noria-MA-*co*-DM[n]$_m$) (Synthesis of Cross-COOH-DM[n]$_m$) [A]. Synthesis of Cross(MMA-COOH-co-DM[6]$_{24}$).

A suspension of Cross(Noria-MA-*co*-DM[6]$_{24}$) in 6 M NaOH aq. was stirred at 120 °C. After 6 h, the insoluble part was collected by filtration, and washed with large amounts of 1 N HCl aq. and water. Figure 1 illustrates the IR spectra of the cross-linking materials before and after the hydrolysis reaction. Peaks at 1741 and 1126 cm^{-1} assignable to C=O and C-O of ester moieties are seen in Figure 1[A]. After hydrolysis, new peaks at 1718 and 1182 cm^{-1} appeared, as shown in Figure 1[B]; these are assignable to carboxylic acid groups. Furthermore, a broad peak at about 3400 cm^{-1}, assignable to -OH groups, is also seen. These results show that hydrolysis proceeded to give a corresponding cross-linking product, Cross-COOH-DM[6]$_{24}$, containing carboxylic acid groups due to removal of noria from Cross(Noria-MA-*co*-DM[6]$_{24}$). The ratio of removal of noria was also investigated. After collection of Cross-COOH-DM[6]$_{24}$ by filtration following the hydrolysis, conc. HCl aq. was added to the filtrate (to pH = 2.0) to precipitate the solid. This was confirmed to be noria by ^{1}H NMR. Thus, the ratio of hydrolysis (RH) could be calculated from the amount of precipitated noria. In the case of Cross-COOH-DM[6]$_{24}$, the values of RH and yield were calculated to be 52 % and 50 %, respectively (Run 6 in Table 2). When Cross(Noria-MA-*co*-DM[6]$_{12}$) was hydrolyzed, the corresponding Cross-COOH-DM[6]$_{12}$ with RH = 12% was obtained in 18% yield (Run 5 in Table 2). In the case of Cross(Noria-MA-*co*-DM[6]$_{2.4}$), the suspension in 12 M NaOH aq. became homogeneous, i.e., all hydrolysis products were soluble, and the corresponding Cross-COOH-DM[6]$_{2.4}$ was not obtained (Run 4 in Table 2). This means that the feed ratio of 2.4 eq. of DM[6] as a cross-linker is too small for the present purpose. Furthermore, in the cases of Cross(Noria-MA-*co*-DM[3]$_m$) (m = 2.4, 12, and 24), only Cross-COOH-DM[3]$_{24}$ with RH = 36% was obtained in 60 % yield, and Cross-COOH-DM[3]$_{2.4}$ and Cross-COOH-DM[3]$_{12}$ were not obtained (Runs 1 ~ 3 in Table 2). When the hydrolysis of Cross(Noria-MA-*co*-DM[24]$_m$) (m = 2.4, 12, and 24) was similarly examined, the corresponding cross-linking products Cross-COOH-DM[24]$_m$ (m = 12 and 24) were obtained in 64 and 96 % yields. However, their values of RH were 9 and 1> %, respectively (Runs 7 ~ 9 in Table 2). These results indicate that hydrolysis of Cross(Noria-MA-*co*-DM[24]$_m$) hardly proceeded, presumably because DM[12] has longer methylene chains that might enhance its hydrophobicity. Thus, hydrolysis reaction of Cross(Noria-MA-co-DM[n]$_m$) depends upon the length of the methylene unit and the amount of DM[n]m cross-linker in the feed.

Notably, Cross-COOH-DM[3]$_{24}$ (RH = 36), Cross-COOH-DM[6]$_{12}$ (RH = 12), Cross-COOH-DM[6]$_{24}$ (RH = 52), and Cross-COOH-DM[12]$_{12}$ (RH = 9) all showed high thermal stability, which was little different from that of the products before hydrolysis (Runs 3, 5, 6, and 8 in Table 2). Among them, Cross-COOH-DM[6]$_{24}$ might be expected to show higher inclusion complex-forming ability with metal ions, because the value of RH (52%, run 5 in Table 2) is higher than those of other cross-linking product, i.e., Cross-COOH-DM[6]$_{24}$ might contain many noria-templated cavities.

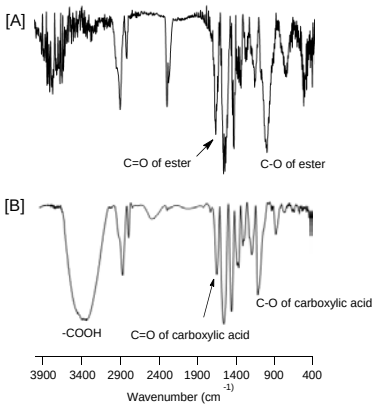


Figure 1. IR spectra of Cross(Noria-MA-*co*-DM[6]$_{24}$) [A] and Cross-COOH-DM[6]$_{24}$ [B].

Table 2. Hydrolysis reaction of Cross(Noria-MA-co-DM[n]$_m$)

Run	Cross(Noria-*co*-DM[n]$_m$)	RH[a] (%)	Cross-COOH-DM[n]$_m$ (%)	T_d[b] (°C)
1	n = 3, m = 2.4	- [b]	- [b]	- [b]
2	n = 3, m =12	- [b]	- [b]	- [b]
3	n = 3, m = 24	36	60	278.8
4	n = 6, m = 2.4	- [b]	- [b]	- [b]
5	n = 6, m =12	12	18	277.2
6	n = 6, m = 24	52	50	275.1
7	n = 12, m = 2.4	- [b]	- [b]	- [b]
8	n = 12, m =12	9	64	323.1
9	n = 12, m = 24	>1	96	- [b]

[a] RH = rario of removal of noria from Cross(Noria-MA-*co*-DM[n]$_m$) [b] Determined by TGA.

Complexation ability of Cross(Noria-MA-*co*-DM[n]$_m$) and Cross-COOH-DM[n]$_m$ with metal ions in aqueous solution

The complex-forming abilities of Cross(Noria-MA-*co*-DM[n]$_m$) and Cross-COOH-DM[n]$_m$ (Scheme 4 [A]) with alkali metal ions such as Na^+, K^+, Rb^+, and Cs^+ were examined by means of liquid-gel extraction studies using the picrate salts of these metals in water. The results are summarized in Table 3.

Table 3. Alkali metal extraction rate of synthesized cross-linking materials[a]

Run	Cross-linking materials	Alkali metal extraction rate (%)			
		Na^+	K^+	Rb^+	Cs^+
1	Cross(Noria-MA-*co*-DM[3]$_{24}$)	20	6	18	12
2	Cross(Noria-MA-*co*-DM[6]$_{24}$)	1>	1>	6	5
3	Cross(Noria-MA-*co*-DM[12]$_{24}$)	3	11	11	7
4	Cross-COOH-DM[3]$_{24}$ (RH = 36)	56	65	41	74
5	Cross-COOH-DM[6]$_{24}$ (RH = 52)	92	94	94	95
6	Cross-COOH-DM[12]$_{24}$ (RH = >1)	1>	18	15	13
7	Cross(MMA-COOH-*co*-DM[6]$_{24}$)	1>	1>	1>	1>

[a] Percentage cation extraction from an aqueous neutral alkali metal ion solution (2.5 x 10^{-4} mol dm^{-3}) in the presence of host cross-linking materials at 25 °C.

Cross(Noria-MA-*co*-DM[12]$_{24}$) and Cross-COOH-DM[12]$_{24}$ showed almost the same inclusion complex-forming abilities in the range between 1> and 18 % (Runs 3 and 6 in Table 3), presumably because the hydrolysis reaction of Cross(Noria-MA-*co*-DM[12]$_{24}$) did not proceed well, as discussed above. However, Cross-COOH-DM[3]$_{24}$ and Cross-COOH-DM[6]$_{24}$ showed higher inclusion complex-forming abilities compared to Cross(Noria-MA-*co*-DM[3]$_{24}$) and Cross(Noria-MA-*co*-DM[6]$_{24}$) (Runs 1, 2, 4, and 5 in Table 3). For comparison, a cross-linking polymer was synthesized by radical polymerization of methylmethacrlate (MMA) and DM[6], followed by hydrolysis reaction to give Cross(MMA-COOH-co-DM[6]) with pendant carboxylic acid groups (Scheme 4 [B]). However, Cross(MMA-COOH-*co*-DM[6]) showed no apparent complex-forming ability with any metal ions examined (Run 7 in Table 3). The remarkable extraction rate of Cross-COOH-DM[6]$_{24}$ suggests that the substantial removal ratio of noria from Cross(Noria-MA-*co*-DM[6]$_{24}$) left many fixed holes that can accommodate metal ions, i.e., noria-templated fixed cavities containing carboxylic acid groups within the cross-linking material. Next, to examine the practical utility of the cross-linking materials, we examined their adsorption properties using a dilute aqueous solution of Cs^+ (100 ppm). The adsorption percentage and adsorption amount are summarized in Table 4. In the case of Cross(Noria-MA-*co*-DM[6]$_{24}$), 5.3 % of Cs^+ was adsorbed, corresponding to 0.12 mmol(+)/g-cross-linking material. The adsorption percentage and adsorption amount of Cross-COOH-DM[6]$_{24}$ were 2.6 % and 0.059 mmol(+)/g-cross-linking material, respectively. Thus, Cross(Noria-MA-*co*-DM[6]$_{24}$) and Cross-COOH-DM[6]$_{24}$ have an adsorption capacity for Cs^+, again supporting the conclusion that Cross-COOH-DM[6]$_{24}$ contains noria-templated cavities lined with carboxylic acid groups, as shown in Scheme 4[A].

Table 4. Adsorption of Cs^+ by Cross(Noria-MA-*co*-DM[6]$_{24}$) and Cross-COOH-DM[6]$_{24}$

Run	Cross-linking material	Adsorption of $Cs^{+a)}$ (%)	Adsorption amount of Cs^+ (mmol(+)/g)$^{a)}$
1	Cross(Noria-MA-*co*-DM[6]$_{24}$)	5.3	0.12
2	Cross-COOH-DM[6]$_{24}$ (RH = 52)	2.6	0.059

[a] cross-linking material s; 0.01 g, 30 ml of aqueous solution at R.T. (100 ppm).

Nitrogen and carbon dioxide adsorption properties of Cross(Noria-MA-*co*-DM[6]$_{24}$) and Cross-COOH-DM[6]$_{24}$ in the solid state

It was reported that noria and noria derivatives adsorb carbon dioxide selectively, due to their central fixed holes[32]. Therefore, we examined the adsorption properties of Cross(Noria-MA-*co*-DM[6]$_{24}$) and Cross-COOH-DM[6]$_{24}$ by measuring the nitrogen and carbon dioxide adsorption isotherms in the solid state. Figure 2 [A] illustrates the nitrogen adsorption at 77K. A rapid increase of adsorbed amount on Cross(Noria-MA-*co*-DM[6]$_{24}$) in the low relative pressure range was observed, suggesting that the cross-linking material might have a microporous structure. Figure 2 [B] shows the results for carbon dioxide at 298K. These results were used to calculate the specific surface areas of the cross-linking materials, as summarized in Table 5. The estimated surface areas of Cross(Noria-MA-*co*-DM[6]$_{24}$) are 292.7 m^2/g (BET, N_2 at 77K) and 264.8 m^2/g (DP, CO_2 at 298K), respectively. On the other hand, the corresponding values of Cross-COOH-DM[6]$_{24}$ were very small: 1.4 m^2/g (BET, N_2 at 77K) and 65.6 m^2/g (DP, CO_2 at 298K). These results indicate that many fixed holes exist in Cross(Noria-MA-*co*-DM[6]$_{24}$), but not in Cross-COOH-DM[6]$_{24}$ in the solid state, i.e., hydrolysis reaction of Cross(Noria-MA-*co*-DM[6]$_{24}$) removed the noria moieties to give the corresponding Cross-COOH-DM[6]$_{24}$ containing many carboxylic acid groups, as shown in Scheme 3. The Cross-COOH-DM[6]$_{24}$ swells in aqueous solution to generate cavities containing carboxylic acid groups, exhibiting high complexation ability with certain metal ions.

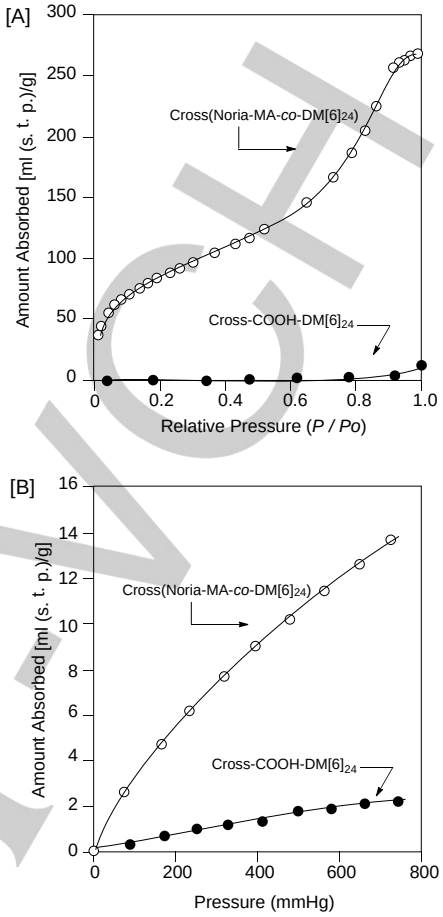


Figure 2. Nitrogen adsorption isotherms at 77K [A] and carbon dioxide adsorption isotherms at 298K [B] for Cross(Noria-MA-*co*-DM[6]$_{24}$) and Cross-COOH-DM[6]$_{24}$.

Table 5. Estimated surface areas of Cross(Noria-MA-*co*-DM[6]$_{24}$) and Cross-COOH-DM[6]$_{24}$

Run	Cross-linking material	Specific surface area [m^2/g]	
		BET(N_2 77K)	DP(CO_2 298K)
1	Cross(Noria-MA-*co*-DM[6]$_{24}$)	292.7	264.8
2	Cross-COOH-DM[6]$_{24}$ (RH = 52)	1.4	65.6

Conclusions

We examined the synthesis and properties of cross-linking materials containing noria moieties and noria-templated fixed cavities with pendant carboxylic acid groups. The radical polymerization of noria derivative noria-MA with pendant methacryloyl groups was performed with certain α, ω-alkanedimethacrylamides (DM[n], n = 3, 6, 12) in the feeds ratios of noria-MA/DM[n] = 1/2.4, 1/12, and 1/24 (m = 2.4, 12, and 24), yielding corresponding cross-linking materials Cross(Noria-MA-

co-DM[n]$_m$), quantitatively. After hydrolysis reaction of Cross(Noria-MA-*co*-DM[n]$_m$), the cross-linking products Cross-COOH-DM[n]$_m$ were obtained by the removal of noria. The inclusion complex abilities was examined using Cross(Noria-MA-*co*-DM[n]$_m$) and Cross-COOH-DM[n]$_m$ in the aqueous some metal salts solution, and it was found that Cross-COOH-DM[6]$_{24}$ has higher absorption abilities with some metals due to higher ratio of hydrolysis (RH = 52%), which have noria-templated cavities containing carboxylic acid groups. In the similar way for the synthesis of Cross-COOH-DM[n]$_m$, the another cross-linking materials containing noria-templated cavities with pendant alcohol or amino groups can be synthesized. Their properties will be reported in the next paper in near future.

Supporting Information Summary

Experimental section and ^{1}H NMR spectrum of noria-MA (Figure S1) were described.

Acknowledgements

This is a product of research which was financially supported (in part) by the Kansai University Fund for Supporting Outlay Research Centers, 2017. “Development of new materials and new processes for establishment of advanced separation system for various metals”.

Keywords: cavity • cross-linking • metal-complexation • noria • synthesis

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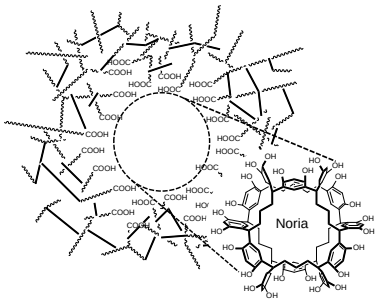

Noria-templated cross-linking material with carboxylic acid

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The synthesis and properties of cross-linking materials containing noria-templated fixed cavities with pendant carboxylic acid groups were examined. Examination of the inclusion-complex-forming ability of the synthesized cross-linking materials using aqueous solutions of metal ions revealed that the synthesized cross-linking materials have the great absorption capacities. These results indicate that they indeed contains noria-templated cavities with pendant carboxylic acids groups that can accommodate metal ions in aqueous solution.