Title	Control of sulfur number in sulfur-containing compounds: the effect of base type, equivalent of the base, and reaction solvent in synthesizing linear sulfur
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Control of sulfur number in sulfur-containing compounds: The effect of base type, equivalent of the base, and reaction solvent in synthesizing linear sulfur

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Since the properties of sulfur-containing compounds depend on the sulfur number contained in the compound, it is desirable to develop a method to control the sulfur number. A common method for synthesizing sulfur-containing compounds is to mix sulfur with a base to form linear sulfur, which is then reacted with an organic compound to obtain a sulfur-containing compound. In this study, we systematically investigated the relationship between the type of base, equivalent amount of the base, and the reaction solvent and the sulfur number in the resulting sulfur-containing compound. The sulfur number of sulfur-containing compounds prepared in water was controlled by the equivalent ratio of elemental sulfur (S_8) and base. Sulfur-containing compound with high sulfur values was obtained using solvents with low dielectric constants and with lower base equivalents compared to S_8.

Keywords: Sulfur, Sulfur-containing compounds

Sulfur is known as molecules that catenate to other than carbon atoms.[1] It has been noted that the properties of persulfide and polysulfide, which are composed of multiple sulfur atoms linked together, change as the number of sulfur atoms varies.[2-4] For example, cysteine persulfide (Cys-SSH), which has one sulfur atom added to cysteine (Cys-SH), is more reactive and acts as an antioxidant.[5] Therefore, it is necessary to conduct systematic studies relating the sulfur number in a compound to its function, and development for controlling the method of the sulfur number in a compound is desired.

Synthesis of compounds containing multiple sulfur atoms is generally synthesized by mixing elemental sulfur (S_8) and a base in solution to form linear sulfur (LS), which is then reacted with a compound having a reactive functional group such as halogen.[6-8] This means that the conditions used to prepare LS determine the sulfur number in the final sulfur-containing compound. In fact, it has been reported that the sulfur number in the resulting sulfur-containing compound varies depending on the ratio of S_8 to sodium and the mixing time when LS is prepared in an anhydrous organic solvent.[9] However, due to the use of hazardous materials such as sodium and anhydrous organic solvents, a simpler LS preparation method is desirable. A simple method to prepare LS by mixing S_8 and a base such as sodium sulfide (Na_2S) in H_2O has been reported.[10-14] However, this method determines the sulfur number in sulfur-containing compounds by the equivalent ratio of S_8 and base, and the actual sulfur umber has not been investigated. To the best of our knowledge, there has been no systematic study of the relationship between reaction conditions and sulfur number in the resulting sulfur-containing compounds. In this study, in

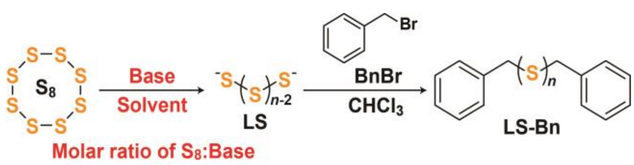

Figure 1. Preparation of LS-Bn.

order to control the sulfur number in sulfur-containing compounds, we report a systematic investigation of the types and equivalents of bases, reaction solvents, and the sulfur number in the resulting sulfur-containing compounds when LS is synthesized from S_8 (Fig. 1).

The sulfur-containing compounds were synthesized by stirring S_8 and a base in a solvent to form LS, followed by the addition of benzyl bromide (BnBr) (LS-Bn, Fig. 1, Scheme S1, and Table S1). The sulfur number in the resulting LS-Bn was evaluated from ^{1}H NMR (Figs. 2 and S1). The protons adjacent to sulfur are known to exhibit different chemical shifts depending on the sulfur number.[9] The sulfur number (n) in the sulfur-containing compounds were determined from the integrated value of these peaks. The validity of the sulfur number in sulfur-containing compounds calculated from this analysis was confirmed because the sulfur number calculated from ^{1}H NMR (n = 4.1) (Table S2) and obtained from elemental analysis (n = 3.9) (Table S3) are similar (Table S4).

We investigated the sulfur number in LS-Bn depending on the type of base used in LS preparation in water, the solvent with the lowest environmental impact (Scheme S2 and Table S5). The bases used were commonly available base, such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium sulfide pentahydrate ($Na_2S{\cdot}5H_2O$),

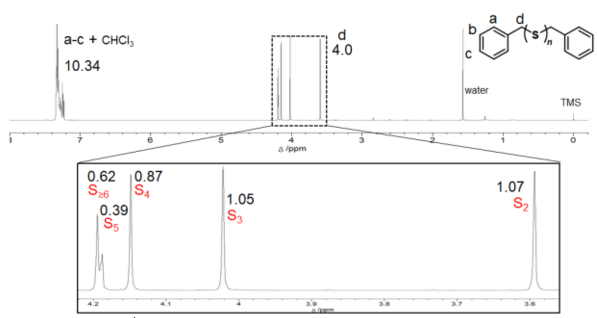

Figure 2. ^{1}H NMR spectrum of LS-Bn in $CDCl_3$ at 25 °C.

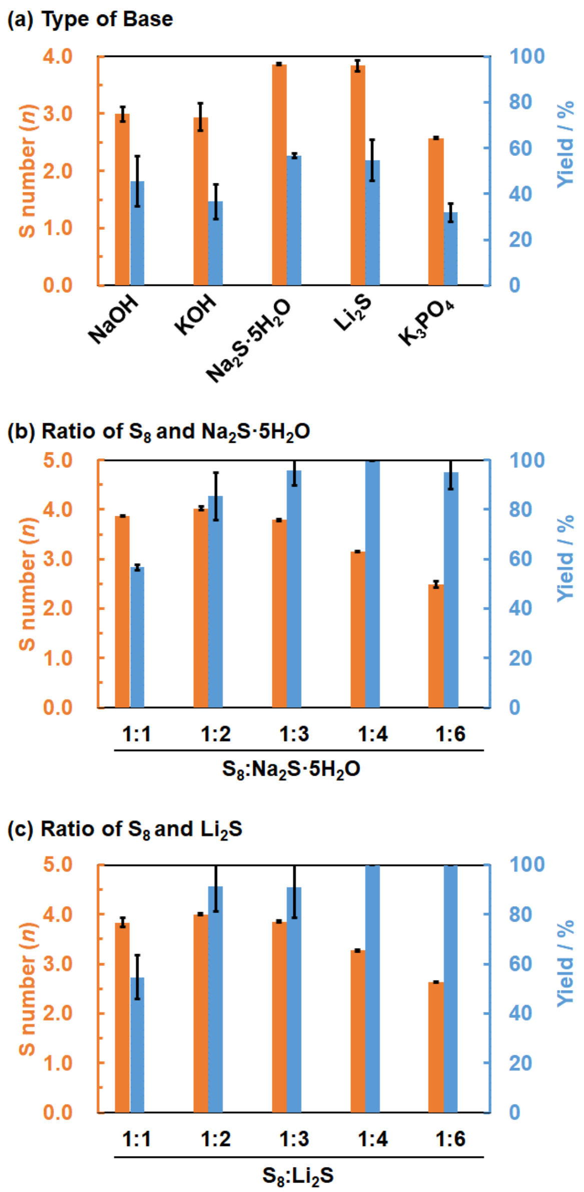

Figure 3. The yield and sulfur number (n) depending on LS prepared in H_2O ((a) Type of base and ratio of S_8 : (b) $Na_2S{\cdot}5H_2O$ or (c) Li_2S).

lithium sulfide (Li_2S), and tripotassium phosphate (K_3PO_4). The equivalent ratios of S_8 and cations (Na, K, and Li) in the bases were fixed at 1:1. The sulfur number (n) for NaOH, KOH, $Na_2S{\cdot}5H_2O$, Li_2S, and K_3PO_4 as bases were 3.0, 2.9, 3.9, 3.8, and 2.6, respectively (Figs. 3a and S2-S6 and Table S6) and $Na_2S{\cdot}5H_2O$ and Li_2S had the highest sulfur number. In the case of $Na_2S{\cdot}5H_2O$ and Li_2S, S^{2-} is used to open the S_8 ring, thus the sulfur in these reagents is incorporated into the LS, resulting in a higher yield and sulfur number in the product. These results suggest that sulfur-containing compounds with high sulfur number are obtained in high yields when appropriate bases are used.

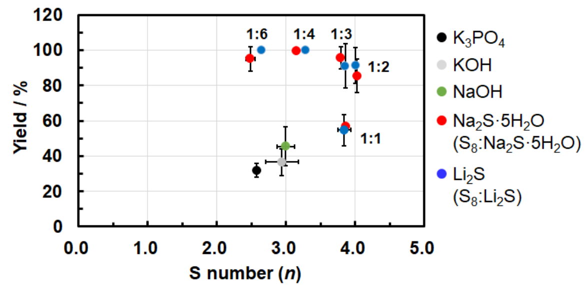

Figure 4. The yield and sulfur number (n) depending on LS synthesis conditions.

The equivalent ratios of $Na_2S{\cdot}5H_2O$ and Li_2S, which had the highest sulfur number in LS-Bn, were further examined (Scheme S3, Figs. S7-S16, and Table S7 and S8). In the case of $Na_2S{\cdot}5H_2O$, when the equivalent ratios of S_8 and Na^+ were 1:1 and 1:2, the sulfur number in LS-Bn was the almost same, while the yield of 1:2 (90%) was higher than that of 1:1 (58%) (Fig. 3b and Table S9). As the equivalent ratio of the base increased, the yield increased and the sulfur number decreased (Fig. 3b and Table S9). This is because the sulfur number in LS was reduced due to the increased number of cations relative to S_8. This behavior was similar for Li_2S (Fig. 3c and Table S10). These results indicate that the average sulfur number in sulfur-containing compounds can be controlled by the type of base and their molar equivalent (Fig. 4).

Solvents were investigated to further improve the sulfur number in the sulfur-containing compounds (Scheme S4 and Table S11). S_8 was dissolved in THF, to which Na_2S (S_8:Na^+ = 1:1 and 1:2) was added and stirred at room temperature before BnBr was added. The sulfur number in LS-Bn was evaluated to be n = 4.4 and 4.3 for 1:1 and 1:2, respectively (Fig. S17 and S18 and Table S12), which are higher than those obtained in H_2O (Fig. 5). This result is consistent with previous papers showing that the lower dielectric constant of the solvent favors the synthesis of sulfur-containing compounds with higher sulfur number.[15] These results indicate that the reaction solvent can also control the sulfur number in sulfur-containing compounds.

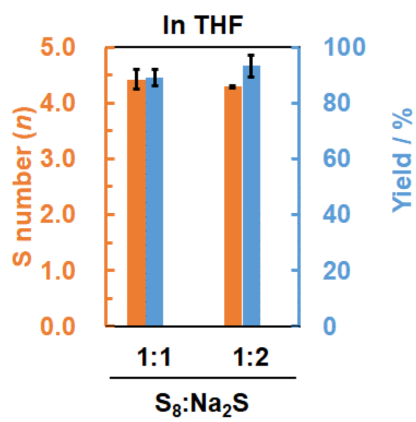

Figure 5. The yield of LS and sulfur number (n) in LS-Bn prepared in THF.

In this study, we systematically investigated the relationship between the reaction conditions, such as base types, their molar equivalents, and reaction solvents, and the sulfur number in the resulting sulfur-containing compounds when synthesizing LS from S_8. The sulfur number of sulfur-containing compounds prepared in water was controlled by the equivalent ratio of S_8 and base. In addition, we also found that using a solvent with a low dielectric constant, such as THF, rather than water, yielded sulfur-containing compounds with even higher sulfur number. The control of sulfur number method is important not only for low-molecular-weight sulfur-containing compounds but also for the sulfur-containing polymers,[16-21] which have recently attracted attention, and is expected to contribute to the creation of functional sulfur polymer materials.

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Supporting Information is available on http://dx.doi.org/10.1246/cl.******.

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Authors' Names(required)	Ryuto Nishimura, Yuichiro Kobayashi, Ryunosuke Kamioka, Shun Hashimoto, Hiroyasu Yamaguchi

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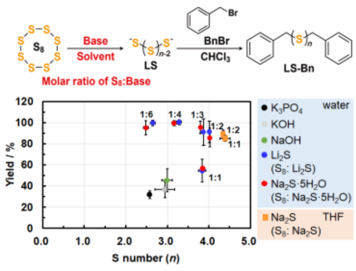

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