J. Chosun Natural Sci.
Vol. 13, No. 2 (2020) pp. 41 – 46
https://doi.org/10.13160/ricns.2020.13.2.41

Synthesis of Allyl Functionalized Silacrown Ethers and Their Application - A Review

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Abstract

A study is reported about the synthesis processes of various silacrown ether by the reaction of alkoxysilanes with polyethylene glycols (PEG) through transesterification. Crown ether-functionalized carbosilane dendrimers and hybrid crown ethers are also discussed. We will also address the solubility enhancement, phase-transfer catalysis of different silacrown as well as their application as Ion-selective electrodes (ISEs) and as active phase of PVC electrodes for the development of potentiometric sensors for detection of alkali-Ions.

Keywords : Silacrown Ethers, Ion-selective electrodes, Dendrimers, Ionophore.

1. Introduction

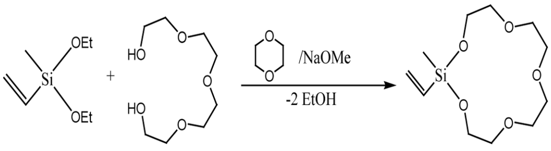
Crown ethers are heterocycles and cyclic oligomers of dioxane that in their simplest form. The essential repeating unit two in dioxane and six in 18-crown-6. The common structure of Silacrowns is $R^1R^2Si(OCH_2CH_2)_nO$. Silacrowns gives ionophoric characters compare to crown ether regarding cation and increase of anionic reactivities[1]. To enhance ionselective electrodes and optodes in polyvinyl chloride (PVC) membranes ion-sensing species are usually immobilized[2].

A crown ether with two silane groups in an endocyclic mode has some advantages. It shows binding capabilities to large cations and can use as phase transfer catalysts which could be used to extract agents of large cations. Some metal ion also can increase the transport efficiency of various silacrown ether.[3] For designing new structures, the structural investigation and their conformational analysis may be useful. Possessing ionophoric properties of new materials these crowns may lead after polymerization[6]. Hybrid disila-Crown ethers with alkali metal was reported in 2016.[7] They shown disilane segments with ethylene in hybrid crown ether complexes on their structural level. It shows that the methyl groups are in eclipsed position where hydrogen at ethylene are staggered position in their arrangement. Dendritic molecules with their highly branched like tree structure show new interest to control the properties like solid surfaces with dendrimers by coating them[8]. For array-based chemical sensor, dendrimers may be suitable due to their various size and chemical composition. The periphery of dendrimers can be made selective which allows metal ion selectivity by transition metal ion with chelating ligands into the microstructures.

We report the synthesis processes of 1-methyl-1-vinyl-14-crown-5, 1,2-Disila crown ether as a model and some promising properties such as electrode properties, solubility enhancement, phase-transfer catalysis. We also addressed their structural level, disilane fragments in hybrid crown ether, carbosilane dendrimers and their application also.

2. Synthesis and Application

The synthesis of silacrowns are prepared by transesterification of alkoxysilanes with polyethylene glycols in presence of catalytic amounts of NaOMe.



Scheme 1. Synthesis method of 1-methyl-1-vinyl-14-crown-5, copied and reprinted from Ref [2]

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(Received : June 11, 2020, Revised : June 14, 2020, Accepted : June 17, 2020)

$$R^1R^2Si(OEt)_2 + HO(CH_2CH_2O)_nH \longrightarrow R^1R^2Si(OCH_2CH_2)_nO + 2EtOH.$$

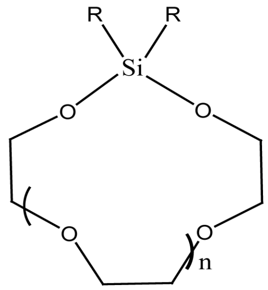


Fig. 1. R is represented a methyl, phenyl or vinyl group, when n=1,2,3,4: sila-11-crown-4, sila-14-crown-5, sila-17-crown-6, sila-20-crown-7[3].

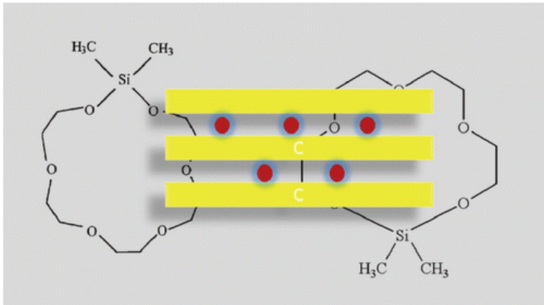


Fig. 2. Hybrid supramolecular materials are prepared by intercalation of two macrocyclic silacrown ethers into montmorillonite layered silicate. Copied with permission from ref[4].

An ethylene bridge of a regular crown ether is substituted by silyl group. Fig. 1 shows the typical reaction of silacrowns. The reaction conditions for dimethoxy or diethoxy silane condensation are much easier because of they are not much sensitive as the di or trichlorosilane reagents. Moreover, it is easier to obtain high molecular weights. On the other hand, the by-product HCl, which is harmful to the product copolymer due to acidic condition where it can be decompose. Through the transetherification reaction of the alkoxysilane with the condensation reaction of dimethoxy or diethoxysilane with PEG was achieved by using the catalyst. Easily by- product can be removed, CH_3OH/C_2H_5OH from the reaction system by distillation.

This process can be expected for new materials to have some efforts upon the ionophoric properties. To promote cyclization in preference to polymerization, transesterification must be selected as the conditions. Alkoxy titanates are generally preferred as catalyst where various materials can be used for the reaction. phase partition, solubility and reactivity of the silacrowns many organic groups (R^1R^2) can be readily substituted distilled from the reaction mixture 80-95% alcohol come out slowly. After distillation at reduced pressure the product can be removed. With moderate viscosity silacrowns are generally odorless, colorless liquids.

Some supramolecular materials are prepared by dimethylsila-14-crown-5 (DMS14C5) and dimethylsila-17-crown-6 (DMS17C6) macrocyclic polyethers into montmorillonite layered silicates[4]. where these will used to prepare Li^+, Na^+ and K^+-montmorillonite intercalation materials which will use as active phase of PVC electrodes for the development of ion-sensing devices. Fig. 2 show the structure of new supramolecular materials are prepared by intercalation of two macrocyclic silacrown.

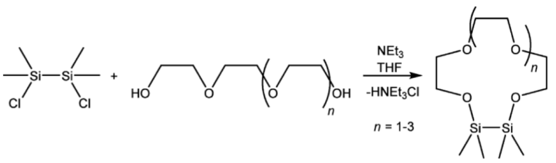
Sila-14-crown-5, sila-17-crown-6, and sila-20- crown-7 have been synthesized. The compounds and yields are given in Table 1. Methyl, vinyl, phenyl, ethyl, and methoxy groups are the substituents on the silicon.[1]

Past few decades Si–O bond has been intensively practiced. Many articles have been published about the unusual short Si–O bond length and the large valence angle of disiloxanes[4]. A crown ether with two silane groups by endocyclic mode has some advantages. It has binding capabilities, act as phase transfer catalyst which can be use as extracting agents for large cations further. Doubly attached analogues of silacrown ether may be the curious subject for their new structures which can be shown by their conformational and structural analysis. Gilles and Hosseini[6] reported new large disilacrown ethers molecules where two diphenylsilane groups are attached by two poiyethyleneglycol chains.

Extraction purposes and for substitution of phenyl groups by hydroxy functionality leading to bis cyclic silanediols which permit next functionalization. In this case, phenyl moieties will enhance the lipophilicity of these components. Kirsten and Hanisch[7] report the synthesis and complexation properties of hybrid crown

Table 1. Silacrowns prepared by transesterification

Compound	bp, ^{0}C ((P, mmHg)	Yield, %
dimethylsila-8-crown-3	90(50)	
dimethylsila-11-crown-4	96(9)	85
dimethylsila-14-crown-5	125-130(0.5)	79
dimethylsila-17-crown-6	168-170 (0.3)	78
dimethylsila-20-crown-7	240-244 (0.2)	73
ethylmethylsila-14-crown-5	130-133 (0.5)	81
vinylmethylsila -14-crown-5	129-131 (0.5)	47
phenylmethylsila-14-crown-5	180-185 (0.1-0.15)	43
vinylmethylsila-17-crown	169-172 (0.3)	54
methoxymethylsila-17-crown-6	170-172 (0.3)	32
dimethylsila-3,6,9-trimethyl-11-crown-4	125-129 (0.2-0.3)	69



Scheme 2. Synthesis route of 1,2-Disila[12] crown-4(n=1), 1,2-Disila-[15]crown-5(n=2), 1,2-Disila-[18]crown-6(n=3), Copied with permission from ref[7].

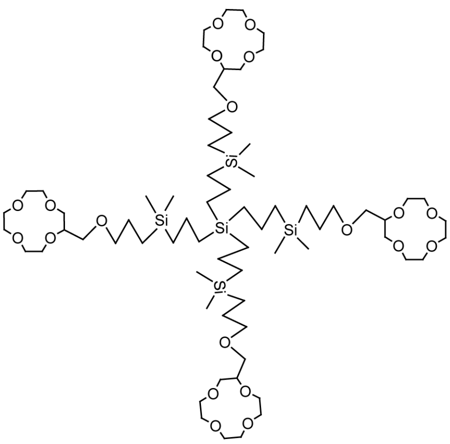


Fig. 3. 2-Dimensitional view of 12-crown-4-modified carbosilane dendrimers. Copied with permission from ref[8].

ethers. Hybrid crown ether consist with disilane and ethylene fragments between the O atom.

In the ligand framework, one disilane unit is inserted by Williamson ether synthesis of 1,1,2,2-tetramethyl-1,2-dichlorodisilane and the corresponding glycol (Scheme 2). Crown ether-functionalized carbosilane dendrimers has been synthesized by roy and lang[7] which can be used as ionophores in chemical sensors. In solid surfaces coating with tree like dendrimers offer new possibilities binding[9] and optical properties[10] which have many potential applications in chemical sensors[11] and photosensitive materials[12].

Solubility enhancement for different silacrown with various salt in acetonitrile was reported by Liotta and Dabdoub.[13] Table 2. shows the solubility data for various inorganic salts in acetonitrile was composed under various conditions.

KBr shows greatest solubility enhancement with sila-20-crown-7. For entering cavity of 18-crown-6 with Potassium ions are often deliberated to have the “just right” diameter. Planar complex does display slight puckering[14]. The cavity of 18-crown-6 is smaller than the potassium ion, steric factors must responsible for a substantial part of the variety in solubility.

Alkali metals in various silacrown ethers show the the rates of transport rate in Table 3. Every value was 15% reproducible with many times experiments where the crown competent ionophores with the capacity to transport metal ions. It also reveals the selectivity patterns monumental of metal ion with the normal crown ethers.

Ion-selective electrodes: Past few decades Ion-selective electrodes (ISEs) have been studied well and now regularly used in industry, environmental areas and clinical purposes for potentiometric measuring of ionic

Table 2. Dimethylsilacrown solubility enhancements

	Salt				
Crown	LiCl	NaBr	KBr	KN_3	KCN
11-4	2: l-4: l	2:2-3 :1	4 :1-5:1		
14-5	6:1-8:1	5:3-6 :1	9: l-11: l		
17-6	3: l-4: l	4: l-5: l	11: l-14: l	18: 1-20: l	10: 1-1 1: 1
20-7			45: 1-50: l		

Solubility enhancements are expressed as ratios of the saturation solubility in 0.15 M silacrown in acetonitrile vs. acetonitrile. Reprinted from Ref [1].

Table 3. Rates of transport of alkali ions using various crown ethers

	Crown rate of transport* 10^8 mol^{-1}/min			
	Na^+	K^+	Rb^+	Cs^+
Si-C-4[a]	2.0	10	3.4	1.5
Si-C-5	5	18	12	7
Si-C-6[b]	35	2700	750	500
Si-C-7[b]	62	840	1200	1000
PMSi-C-5[c]	5	12	e	E
HEG[d]	8	190	210	170
PEM	5	330	21	10
TEG	2	5	e	e

[a]Si-C-4, Si-C-5, Si-C-6, Si-C-7 are the dimethylsilacrowns. All ionophores at 10^{-2} mol/l. Phenylmethylsilacrowns-5[c] and [d]hexa-, penta- and tetraethyleneoxy glycol respectively. Reported with permission of ref [3].

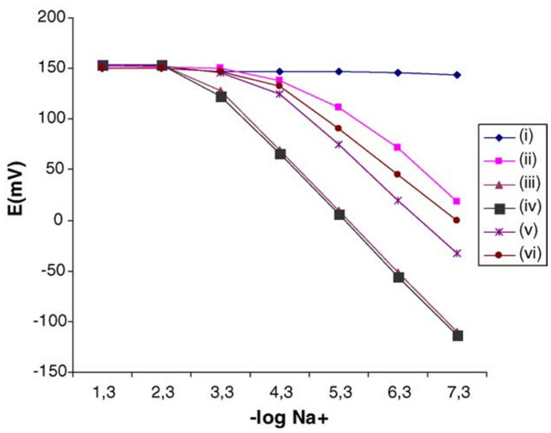


Fig. 4. Potential response of sodium sensor based on different composition of with 1-methyl-1-vinyl-14-crown-5. Reprinted from Ref[2].

species[15,16]. Dynamic response of Ion-selective electrode is produced by selective complexation of the ion by ionophores dispersed in a poly (vinylchloride) (PVC) matrix. PVC easily select sensory elements based on their size of the ion in clinical and environmental assays[17]. 1-methyl-1-vinyl-14-crown-5 shows electrode and membrane optimization properties of the Na+-selective polymeric membrane electrode[2].

Selectivity and sensitivity depend on ionophore as well as membrane composition and additives. So, Na^+-ISE membrane is best for these purposes. Table 3 and Fig. 4 show the results about various membrane made with 1-methyl-1-vinyl-14-crown-5 as active phase and having the plastisizer with an anion excluder show the best working concentration of 3.16×10^{-6} to 1.1×10^{-1}M with a slope of 55.0 mv per decade.

Silacrown-based intercalation compounds are made after modification with PVC membranes, where it has a protective effect on the ionophore, which is impeding from the membrane.

In this case, Na^+-montmorillonite have been used for the preparation of intercalation compounds to evaluate. In aqueous solutions of LiCl, NaCl or KCl in concentrations ranging from 10^{-6} to 10^{-1} M, this PVC membrane electrodes have been examined where Fig. 5 show the result of potentiometric curves which is positive slope in the linear range.

However, this data show subnerstian responses which gives slope values below the theoretical value of +59 mV/decade for the cations. To construct the electrode and the preparation of the intercalation materials, this data suggests an improvement which could increase the electroanalytical performance of the sensors.

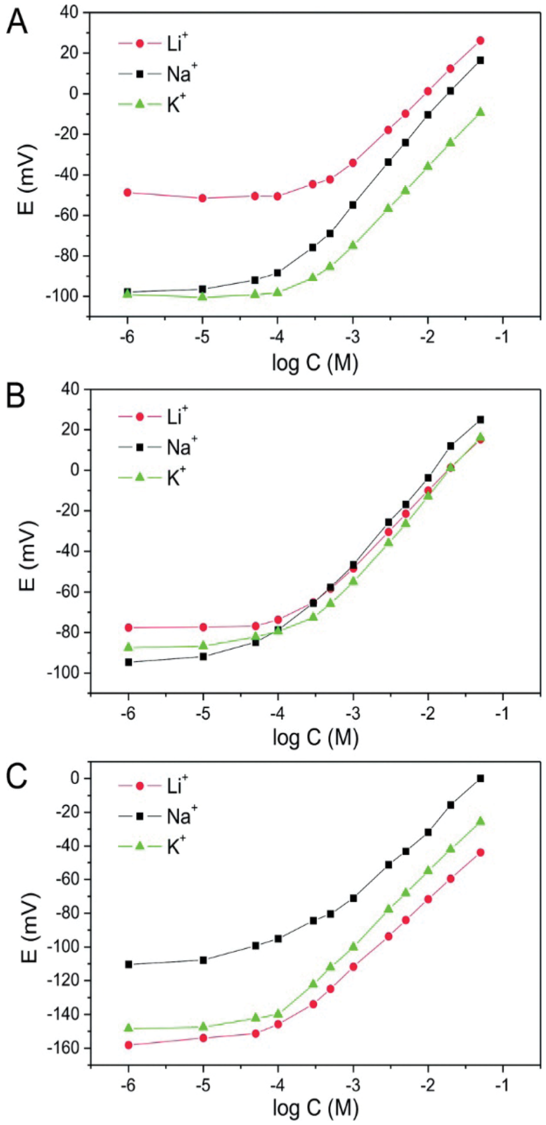


Fig. 5. Potentiometric response of sensor based on different PVC electrodes after modification with (A) Dimethylsila 17C6/mont-Na, (B) Dimethylsila 14C5/mont-Na and (C) 18C6/mont-Na towards K^+, Li^+, and Na^+ cations. Reprinted from Ref [4].

3. Conclusion

Silacrown and their analouges like disilacrown, hybrid silacrown has been studied. We discussed different processes of synthesis methods and properties where extraction abilities, binding properties of cations are yet to described. Disilacrown can be studied in phase transfer catalysis area. Silacrown ethers have the advantages of efficient ionophoric character as short term transport of long-term side effect. The importance of differe nt silacrown ether which was synthesized recently use as industrial additives and synthesizing of such kinds of molecules for the pharmacological sectors is an attractive goal also.

Acknowledgments

Following are results of a study on the “Leaders in Industry-university Cooperation +” Project, supported by the Ministry of Education and National Research Foundation of Korea.

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