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Synthesis of amphiphilic silane coupling agents based on poly(2-ethyl-2-oxazoline) and their reactions with tetraethoxysilane

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Summary

Ring-opening polymerization of 2-alkyl-2-oxazoline (alkyl=ethyl, *n*-butyl, *n*-octyl) was carried out with an initiator of methyl tosylate followed by the treatment with 3-aminopropyltriethoxysilane to produce a novel type of polymeric silane coupling agents. Similarly, telechelic triethoxysilyl-terminated poly(2-alkyl-2-oxazoline)s were prepared by using a bifunctional initiator. The molecular weights of the produced polymers could be effectively controlled by the feed ratio of the initiator to the monomer. These end-functionalized polymers were reacted with tetraethoxysilane with an acid catalyst by the sol-gel method. In the case of poly(2-ethyl-2-oxazoline), a homogeneous and transparent polymer hybrid was obtained. This polymer hybrid absorbed both of water and organic solvents, which showed amphiphilic adsorption property.

Introduction

In these several decades, we have explored the chemistry of polyoxazoline. [3] Generally, polyoxazolines cover a wide spectrum from hydrophilic to lipophilic nature depending on the *N*-acyl groups. [4] It should be also noted that ring-opening polymerization of 2-oxazolines is known to proceed in living mechanism under the appropriate conditions. By using this living nature of polymerization, we have recently reported a novel type of polymeric silane coupling agents based on poly(2-methyl-2-oxazoline). [5] This polymer was used to modify the surface of silica gel hydrophilic. In addition, triethoxysilyl-terminated poly(2-methyl-2-oxazoline) was copoly-condensed with tetraethoxysilane to form a homogeneous and transparent polymer hybrid, which absorbed water. [6] In this paper, we describe the preparation of triethoxysilyl-terminated polymers on the basis of 2-alkyl-2-oxazolines (alkyl=ethyl or higher) and the reaction with tetraethoxysilane by the so-called sol-gel method. The adsorption properties of the obtained polymer hybrids were also examined by swelling in water and various organic solvents.

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Footnotes 1 and 2, see references

Experimental

Materials and Instruments. 2-Ethyl-2-oxazoline (**1a**), methyl p-toluenesulfonate (methyl tosylate), 3-aminopropyltriethoxysilane (**2**) and acetonitrile were dried and distilled under nitrogen. Tetraethoxysilane and methanol were used as received without purification. 2-*n*-Butyl-2-oxazoline (**1b**), 2-*n*-octyl-2-oxazoline (**1c**) and bifunctional initiator (**4**) were prepared according to the method reported previously. [7]

IR spectrum was obtained on a Hitachi 260-50 grating spectrometer. ^{1}H-NMR spectrum was recorded in $CDCl_3$ on a Hitachi R-600 (60MHz) instrument. Gel permeation chromatographic (GPC) analysis was carried out on a Tosoh CCPD (TSK gel G2500) after calibration with standard poly(*N*-acetylethylenimine) samples. Thermogravimetric analysis (TGA) was made on a Shimadzu DT-30 instrument under nitrogen stream.

Synthesis of Triethoxysilyl-Terminated Poly(2-ethyl-2-oxazoline) (3a). Under nitrogen, a mixture of **1a** (4.71g, 47.5mmol), methyl tosylate (0.99g, 5.34mmol) and acetonitrile (30ml) was placed in a 100ml flask equipped with a reflux condenser and stirred at 80°C for 10h. To the reaction mixture was added **2** (1.42g, 6.40mmol) at 0°C. The resulting solution was stirred at room temperature for 2 days followed by the treatment with an ion-exchange resin (Amberlyst A-21). Triethoxysilyl-terminated poly(2-ethyl-2-oxazoline) (**3a**) was isolated by reprecipitation from chloroform to *n*-hexane and dried *in vacuo*. Yield was 5.23g (89%).

Triethoxysilyl-terminated poly(2-*n*-butyl-2-oxazoline) (**3b**) or poly(2-*n*-octyl-2-oxazoline) (**3c**) was prepared by polymerization of **1b** or **1c** using a similar manner.

Telechelic Triethoxysilyl-Terminated Poly(2-ethyl-2-oxazoline) (5a). A mixture of **4** (1.09g, 1.92mmol), **1a** (2.39g, 24.1mmol) and acetonitrile (15ml) was placed in a 50ml flask equipped with a reflux condenser and heated at 80°C for 9.5h. Addition of **2** (1.32g, 5.94mmol) was followed by the treatment with an ion-exchange resin to give telechelic triethoxysilyl-terminated poly(2-ethyl-2-oxazoline) (**5a**), which was purified by reprecipitation from chloroform to *n*-hexane. Yield was 2.64g (76%).

Copolycondensation of 3a or 5a with Tetraethoxysilane. **3a** (3.06g) and tetraethoxysilane (3.08g) were dissolved in methanol (5ml). 1N HCl (3.43g) was added and the reaction mixture was allowed to stand at room temperature for several days. After the solvent vaporized, the remained glassy silica gel was purified by Soxhlet extraction with chloroform.

Other triethoxysilyl-terminated poly(2-alkyl-2-oxazoline)s (**3b** and **3c**) were similarly reacted with tetraethoxysilane.

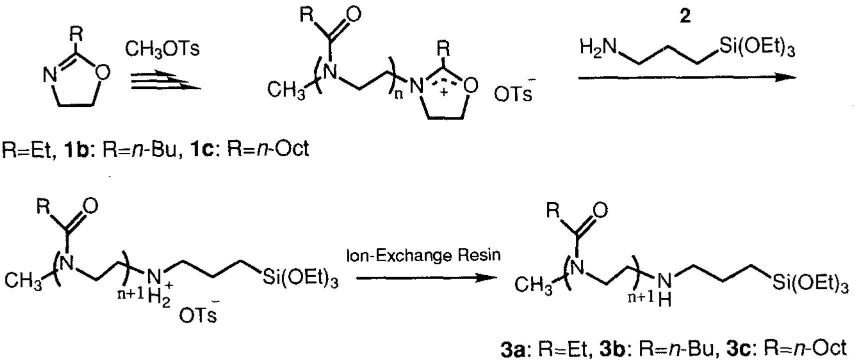
Results and Discussion

Synthesis of Poly(2-alkyl-2-oxazoline) Silane Coupling Agents (3a-3c, 5a-5c). Ring-opening polymerization of 2-oxazolines proceeds in living mechanism under the appropriate conditions. [3] This living nature ensures the effective introduction of the functional group at the end of polyoxazoline. As shown in Scheme 1, ring-opening polymerization of 2-ethyl-2-oxazoline (**1a**) was carried out using methyl tosylate as an initiator. The propagating oxazolinium end group was then reacted with 3-aminopropyltriethoxysilane (**2**) followed by the treatment with a basic ion-exchange resin to remove p-toluenesulfonic acid. Thus, triethoxysilyl group was introduced effectively at the end of poly(2-ethyl-2-oxazoline). Each step of this conversion was found to proceed quantitatively from the results of ^{1}H-NMR spectra.

Triethoxysilyl-terminated poly(2-*n*-butyl-2-oxazoline) (**3b**) and poly(2-*n*-octyl-2-oxazoline) (**3c**) were also prepared by ring-opening polymerization of 2-*n*-butyl-2-oxazoline (**1b**) or 2-*n*-octyl-2-oxazoline (**1c**), respectively. In all cases, the molecular weights of the obtained polymeric silane coupling agents were effectively controlled by the feed ratio of the initiator (methyl tosylate) to the monomer (**1a**-**1c**). From the results of ^{1}H-NMR spectra of the product polymers, it is found that the functionality of the end triethoxysilyl group was nearly unity.

Scheme 2 represents a preparative way for the telechelic triethoxysilyl-terminated poly(2-alkyl-2-oxazoline) silane coupling

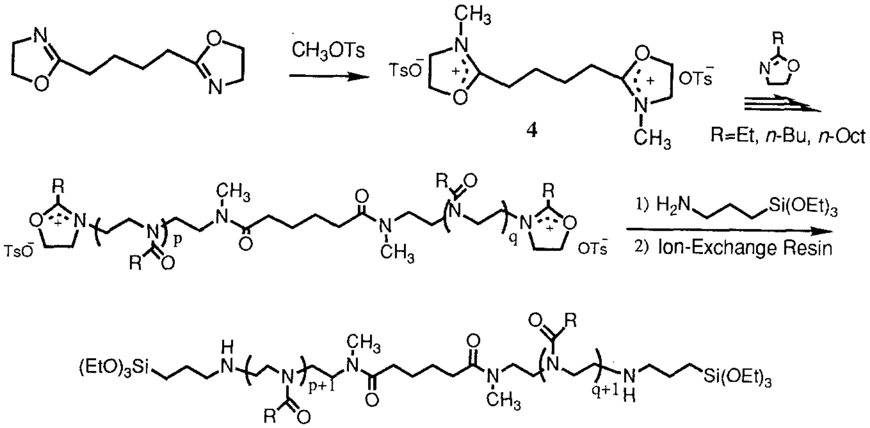
Scheme 1



1a: R=Et, **1b**: R=*n*-Bu, **1c**: R=*n*-Oct

3a: R=Et, **3b**: R=*n*-Bu, **3c**: R=*n*-Oct

Scheme 2



5a: R=Et, **5b**: *n*-Bu, **5c**: *n*-Oct

Table I. Synthesis of Polyoxazoline Silane-Coupling Agents.

Run	Polymer	Time(h)	Yield(%)	D.P.[a]
1	**3a**	5	59	3.3
2	**3a**	10	89	9.5
3	**3a**	10	96	14.5
4	**3b**	5	94	7.6
5	**3c**	9	67	3.3
6	**3c**	8	73	6.0
7	**5a**	9.5	76	16.0
8	**5b**	7.5	47	20.0
9	**5c**	14	75	10.3

a) Degree of polymerization was calculated from ^{1}H-NMR.

agents (**5a**-**5c**). In this polymerization, the bifunctional initiator (**4**) was used to give poly(2-alkyl-2-oxazoline) having two oxazolinium propagating groups at both ends. The same treatment of this polymer with **2** as described above produced the telechelic functionalized poly(2-alkyl-2-oxazoline)s (**5a**-**5c**).

The results of the preparation of monofunctional (**3a**-**3c**) and bifunctional (**5a**-**5c**) poly(2-alkyl-2-oxazoline) silane coupling agents are summarized in Table I, in which the degree of polymerization was calculated from ^{1}H-NMR. Poly(2-alkyl-2-oxazoline) silane coupling agents were thus obtained in high yields. Similarly to the preparation of **3a**-**3c**, the molecular weights of **5a**-**5c** could be again controlled by the feed ratio of the initiator (**4**) to the monomer (**1a**-**1c**).

Copolycondensation of Poly(2-alkyl-2-oxazoline) Silane Coupling Agents (3a-3c, 5a-5c) with Tetraethoxysilane by the Sol-Gel Method. Poly(2-alkyl-2-oxazoline) segments were introduced into silica matrix by copolycondensation of poly(2-alkyl-2-oxazoline) silane coupling agents with tetraethoxysilane. An acid catalyst was used for this sol-gel reaction. The homogeneous and transparent polymer hybrid was obtained by this procedure starting from poly(2-ethyl-2-oxazoline) (**3a** or **5a**). Polyoxazolines having higher alkyl groups (**3b**, **3c**, **5b**, **5c**), however, gave turbid glasses due to phase-separation during the sol-gel process. For the preparation of homogeneous polymer hybrids of poly(2-methyl-2-oxazoline), hydrogen bonding between amide carbonyl groups and silanol groups of silica gel was found to play an important role. [6] In the cases of higher alkyl polyoxazolines in the present study, the interaction through hydrogen bonding should be not enough for high dispersion of polyoxazoline segments into silica matrix.

Swelling Property of Poly(2-alkyl-2-oxazoline)-Modified Silica Gel. Table II summarizes the results of adsorption properties of poly(2-alkyl-2-oxazoline)-modified silica gels. As shown

Table II. Adsorption Property of Poly(2-alkyl-2-oxazoline)-Modified Silica Gels.

Run	Polyoxazoline		P/Si[b]	wt loss (%)[c]	Adsorption Property[d] (Solvent)				
		D.P.[a]			H_2O	*n*-PrOH	DMF		Toluene
1	**3a**	5.3	1/10	43	241	64	155	23	32
2	**3a**	11.7	1/2	40	143	16	36	16	20
3	**3a**	11.7	1/5	49	200	111	110	15	11
4	**3a**	11.7	1/10	40	214	52	120	59	54
5	**3b**	7.7	1/5	42	146	22	49	14	19
6	**3c**	12.5	1/5	18	54	4	11	0	0
7	---	---	---	---	119	8	16	12	15

a) Degree of polymerization.
b) Feed ratio of polyoxazoline to tetraethoxysilane.
c) Weight loss was determined by TGA (at 600°C).
d) (W'/W)x100, W'=weight of absorbed solvent, W=weight of dried gel.

in this table, polymer hybrids prepared from **3a** absorbed water and also organic solvents such as DMF or *n*-propanol. This result means that the obtained polymer hybrid, especially that from **3a**, in this study shows the amphiphilic adsorption property.

References and Notes

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