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AN ORGANIC/INORGANIC HYBRID POLYMER

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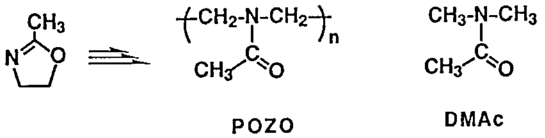
ABSTRACT

Poly(*N*-acetylethylenimine) (polyoxazoline) (POZO) with a terminal triethoxysilyl group was successfully synthesized by the ring-opening polymerization of 2-methyl-2-oxazoline followed by termination with 3-aminopropyltriethoxysilane. Triethoxysilyl-terminated telechelic POZO was prepared by using a bifunctional initiator. These silane coupling POZOs were subjected to acid-catalyzed cohydrolysis polymerization with tetraethoxysilane by the so-called "sol-gel" method to produce a novel organic/inorganic hybrid polymer (block copolymer), which was a homogeneous transparent/glassy composite material. The obtained hybrid showed higher hydrophilic properties compared with silica gel without POZO segments. On the other hand, a hybrid polymer consisting of poly(2-ethyl-2-oxazoline) and silica gel, which absorbed both water and organic solvents, showed amphiphilic properties. POZO segments were eliminated by pyrolysis of the present hybrid polymer to produce a silica with micropores.

INTRODUCTION

We have studied the ring-opening polymerization of 2-methyl-2-oxazoline for several years [1]. The resulting poly(*N*-acetylethylenimine) (polyoxazoline) (POZO) can be regarded as a polymer homolog of *N*,*N*-

dimethylacetamide (DMAc). It is well known that DMAc shows unique characteristics with its strong affinity for water and its solubilizing ability for various organic commodity polymers. Similarly, POZO has been shown to possess high hydrophilicity and compatibility with organic polymers [2]. The ring-opening polymerization of 2-methyl-2-oxazoline is known to be clean, i.e., no chain transfer and termination reactions under appropriate conditions. This makes it possible to prepare block copolymers with the desired molecular weights and composition and also to introduce a reactive functional group at the end of POZO. On the basis of these properties of POZO, we have explored novel functional polymers of nonionic polymeric surfactants [3] and nonionic hydrogels [4, 5].



We reported earlier that trimethoxysilyl-terminated POZO, as a novel silane coupling agent, was reacted with the silanol group at the surface of silica gel to make its surface hydrophilic [6].

On the other hand, a considerable amount of research has been done with the so-called "sol-gel" method by which a metal oxide matrix can be prepared under mild conditions. In general, a metal oxide may be regarded as a three-dimensional inorganic polymer network consisting of metal-oxygen bonds. Thus, the sol-gel reaction makes it possible to incorporate organic polymer segments in the network matrix of an inorganic polymer. Mark et al. reported the reinforcement of polysiloxane networks by the *in-situ* precipitation of silica [7–9]. Wilkes and coworkers studied novel hybrid materials consisting of silica gel and poly(dimethylsiloxane) or of silica gel and poly(tetramethylene oxide) [10, 11]. The material obtained showed good optical transparency and a very different mechanical behavior compared with that of pure sol-gel glasses.

Here we report a combination of POZO and sol-gel glass at the molecular level, termed a "hybrid polymer," and which consists of segments of organic (POZO) and inorganic (silica) polymers. This hybrid polymer is expected to show novel and promising properties based on the characteristics of POZO as described above. We also suggest a novel methodology for the preparation of microporous silica by means of the pyrolysis of a hybrid polymer.

POZO SILANE COUPLING AGENT VIA RING-OPENING POLYMERIZATION OF 2-METHYL-2-OXAZOLINE

Triethoxysilyl-terminated POZO was prepared by the ring-opening polymerization of 2-methyl-2-oxazoline, followed by treatment of the resulting oxazolinium propagating end-group with 3-aminopropyltriethoxysilane (APTS) (Scheme 1). The complete transformation reactions in Scheme 1 were examined by ^{1}H-NMR spectra, which showed the integral ratios were in good agreement with the expected structures.

On the other hand, by using a bifunctional initiator, triethoxysilyl groups were introduced at the α- and ω-positions of POZO after treatment of the telechelic oxazolinium end-groups with APTS (Scheme 2). The results of the preparation of POZO silane coupling agents are summarized in Table 1. In all cases the conversions were almost quantitative and the molecular weights of the silane coupling agents obtained were easily controlled by the feed ratio of initiator and monomer.

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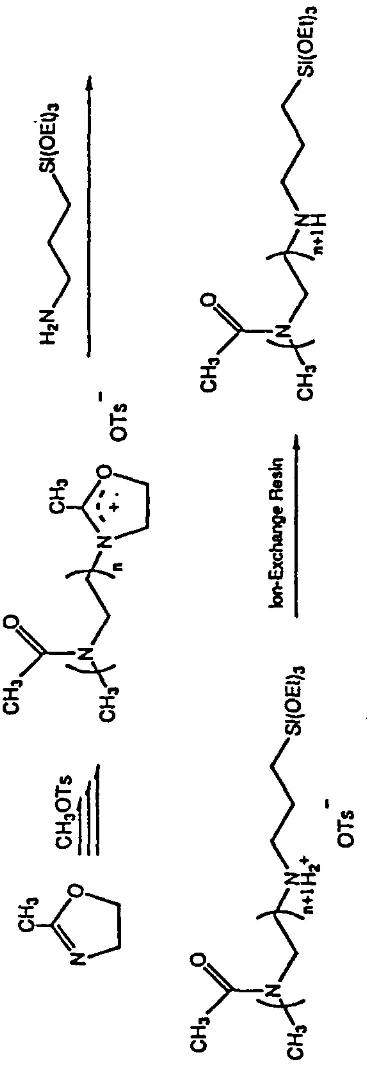
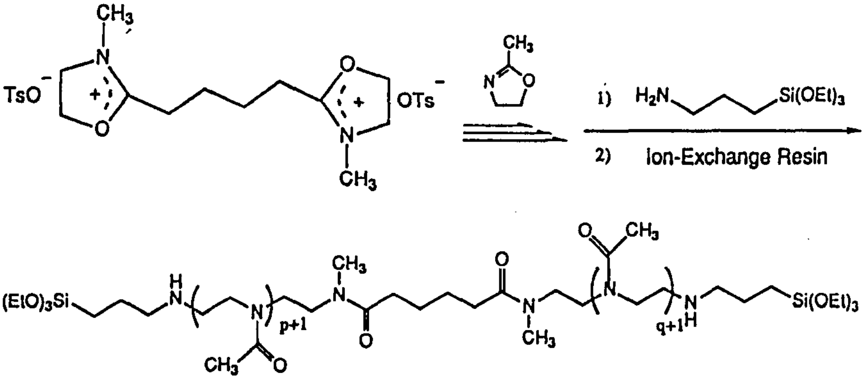
As illustrated in Scheme 3, the acid-catalyzed cohydrolysis of triethoxysilyl-terminated POZO and tetraethoxysilane produced the POZO-modified silica gel, which was homogeneous and transparent. The telechelic POZO segments were connected through their α- and ω-positions to the silica matrix. The homogeneity of the composite gel obtained may be due to chemical bonding at the end of POZO and to the interaction between the amide group in POZO and silica through hydrogen bonding. This explanation is illustrated in Fig. 1. In other words, a molecular level combination between organic polymer (POZO) and inorganic polymer (silica) has been accomplished, for which the terminology “organic/inorganic hybrid polymer” is proposed.

The gels obtained were purified by Soxhlet extraction with chloroform to remove the unreacted POZO. The results of the preparation of hybrid polymers are summarized in Table 2 together with their water adsorptions. Compared with the silica gel without POZO segments, the modified silica with 50% POZO was found to show higher water adsorption.

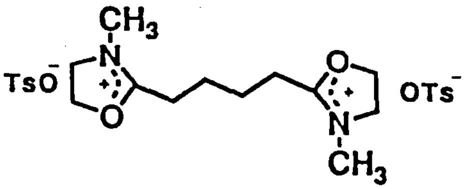

CH3
N
O
CH3OTs
CH3
O
N
CH3
n
CH3
O
N
+
OTs
H2N
Si(OEt)3
CH3
O
N
CH3
n+1
H2+
N
Si(OEt)3
OTs
Ion-Exchange Resin
CH3
O
N
CH3
n+1
H
N
Si(OEt)3

SCHEME 1.

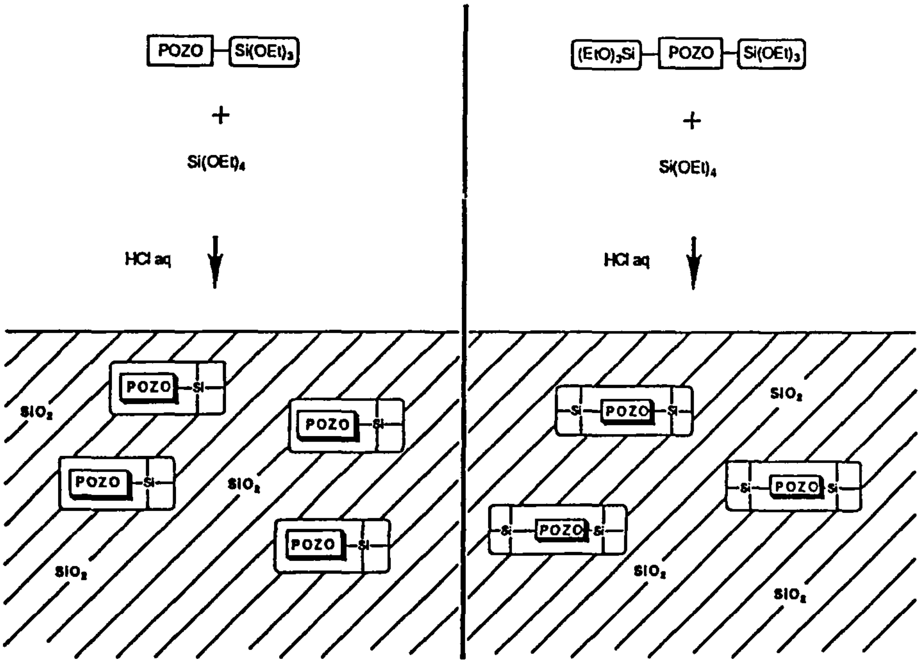


SCHEME 2.

TABLE 1. Preparation of Triethoxysilyl-Terminated POZO[a]

Run	Initiator	Time, h	Yield, %	$\overline{M}_n$[b]
1	CH_3OTs	5	66	510
2	CH_3OTs	11	100	1040
3	CH_3OTs	10	100	1610
4		8.5	84	1960

[a] In CH_3CN, 880°C.
[b] Calculated from ^1H NMR.



SCHEME 3.

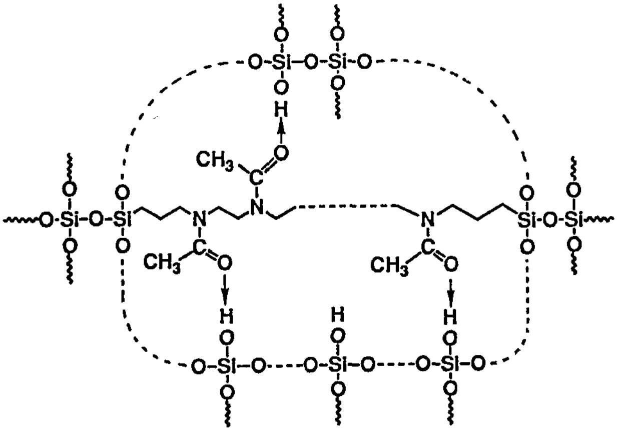


FIG. 1.

TABLE 2. Preparation and Water Adsorption Property of POZO-Modified Silica Gel

Run	POZO (*DP*)[a]	POZO/ $Si(OEt)_4$	Weight loss (TGA), %	POZO, wt%[b]	H_2O content[c]
1	 [d]	1/2	49.0	50.0	2.98
2	(9.0)	1/10	29.4	15.6	1.87
3		1/2	47.5	47.2	2.26
4	(14.4)	1/10	27.3	14.2	1.63
5		1/2	50.3	53.1	3.46
6	(16.1)	1/10	28.5	17.9	1.92
7		0	18.2	0	1.53

[a] Calculated from feed ratio.

[b] Calculated from elemental analysis.

[c] g wet gel/g dried gel.

[d] O = $Si(OEt)_3$.

AMPHIPHILIC SILICA GEL

Generally, polyoxazolines can vary from hydrophilic to lipophilic, depending on their *N*-acyl groups. By using a method similar for 2-methyl-2-oxazoline to that described above, various silane coupling agents were prepared by ring-opening polymerizations of 2-oxazolines (2-ethyl-, 2-*n*-butyl-, and 2-*n*-octyl-2-oxazoline) followed by treatment of the propagating oxazolinium living end with APTS. These results are summarized in Table 3. The molecular weights of the obtained silane coupling agents based on poly(2-alkyl-2-oxazoline)s (PROZO) were again controlled by the feed ratios.

These polymers were copolycondensed with tetraethoxysilane by an acid catalyst to produce PROZO-modified silica gel. The composite gel

TABLE 3. Synthesis of $(EtO)_3Si$-PROZO[a]

Run	R	$[M]_0/[I]_0$[b]	Polymerization time, h	Yield, %	$\overline{DP}$[c]
1	Et	5.0	5	94	5.3
2	Et	7.1	5	63	6.9
3	Et	9.0	16	75	11.7
4	^{n}Bu	6.8	18	100	7.7
5	^{n}Bu	7.0	5	94	7.6
6	^{n}Oct	2.8	9	67	3.3
7	^{n}Oct	7.1	8	73	6.0
8	^{n}Oct	8.1	15	80	12.5

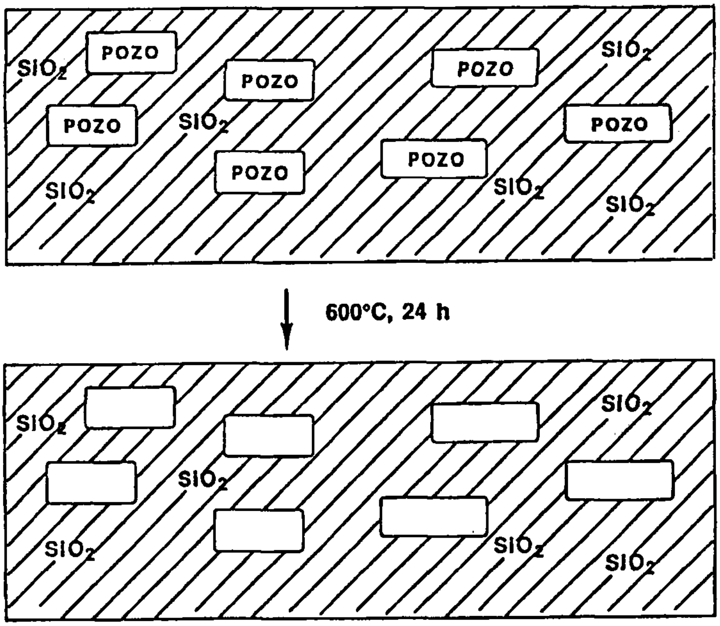
[a] At 80°C.
[b] [M] = [2-alkyl-2-oxazoline], [I] = [MeOTs].
[c] ^{1}H NMR.

from 2-ethyl-2-oxazoline was homogeneous and a transparent glass, similar to that from 2-methyl-2-oxazoline. As summarized in Table 4, PROZO-modified silica gels, especially gels based on poly(2-ethyl-2-oxazoline), absorb both water and organic solvents such as DMF and alcohols. This means that the composite gel has amphiphilic adsorption properties.

TABLE 4. Adsorption Property[a] of PROZO-Modified Silica Gel

Run	POZO	$\overline{DP}$	P/S[b]	Weight loss, %	Solvent				
					H_2O	DMF	*n*-PrOH	$\widehat{Cl\ Cl}$	Toluene
1	Et	5.3	1/10	43	241	155	64	23	32
2	Et	11.7	1/2	40	143	36	16	16	20
3	Et	11.7	1/5	49	200	110	111	15	11
4	Et	11.7	1/10	40	214	120	52	59	54
5	^{n}Bu	7.7	1/5	42	146	49	22	14	19
6	^{n}Oct	12.5	1/5	18	54	11	4	0	0
7	—	—	—	—	119	16	8	12	15

[a] $(w' - w)/w \times 100$. w' = weight of swollen gel, w = weight of dried gel.
[b] $POZO/Si(OEt)_4$.



SCHEME 4.

PYROLYSIS OF HYBRID POLYMER

POZO segments can be eliminated by the pyrolysis of the present hybrid polymer, i.e., the pyrolysis of the POZO-silica hybrid polymer at a temperature below the fusion point of silica gel produces a silica having micropores, as illustrated in Scheme 4. For example, a porous silica with an 800 m^2/g surface area and a 0.5 cm^3/g pore volume was produced from the POZO-silica hybrid polymer by this procedure. The pore volume and surface area of microporous silica could be controlled by the POZO content present in the hybrid state before pyrolysis.

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