

Synthesis of poly(silyl ether) by the addition reaction of bisphenol-S diglycidyl ether and dichlorodiphenylsilane

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In this study, a new poly(silyl ether) with reactive pendant chloromethyl groups was synthesized by an addition reaction between dichlorodiphenylsilane (CPS) and the diglycidyl ether of bisphenol-S (bisphenol-S epoxy). The polyaddition proceeded very smoothly and regioselectively in toluene catalysed by quaternary ammonium or phosphonium salts such as tetrabutylammonium bromide, tetrabutylammonium fluoride and tetrabutylphosphonium bromide to produce a polymer with high molecular weight. The polyaddition also proceeded using triphenylphosphine as a catalyst to afford the poly(silyl ether), but with low molecular weight. On the other hand, the reaction did not occur without a catalyst under the same reaction conditions. Also, the nature of the catalyst and the reaction solvent influenced the polymer's yields and molecular weights. The glass transition temperature of poly(silyl ether) was 68°C and the X-ray diffraction pattern revealed that the polymer was semi-crystalline. Furthermore, experimental results indicated that the subsequent poly(silyl ether) based on bisphenol-S with reactive pendant chloromethyl groups exhibited excellent solubility in common organic solvents. © 1997 Elsevier Science Ltd.

(Keywords: poly(silyl ether); bisphenol-S; polyaddition)

INTRODUCTION

Polymers with a silicon or sulfonyl group in the main chain are noteworthy as high-performance materials. For instance, silicon-containing polymers have been extensively studied for multilayer resist systems and contrast enhancement lithography, since they provide the resistance to oxygen-reactive ion etching and adhesion to a variety of resistance materials¹. Poly(siloxane)s² with a low temperature flexibility and high temperature stability have been widely used as elastomers and plastics in various industries. Recently, attention has increasingly focused on polysilanes due to their scientific and application importance in the field of electronics and optoelectronics^{3,4}. Polysilanes have also been found to be useful materials for medical applications due to such characteristics as good transparency, oxygen permeability and flexibility.

Poly(silyl ether)s are among the most interesting new silicon polymers and have been synthesized by polycondensation of dichlorosilanes^{5,6}, diphenoxysilanes⁷ or diaminosilanes^{1,7} with various diols. However, previous investigations involving the synthesis of poly(silyl ether)s by the addition of bis(epoxide)s with dichlorosilanes are relatively scarce. Nishikubo and co-workers^{8,9} reported that polyaddition of bis(epoxide)s with diacyl chlorides or active diesters proceed smoothly and regioselectively using quaternary onium salts or crown ether complexes as catalysts to produce the corresponding polyesters. Poly(silyl ether)s^{10,11} with high molecular weights were

also synthesized by the polyaddition of bis(epoxide)s with dichlorosilanes. In addition, one of the approaches to improve solubility of the polymers without loss of their high thermal stability is the introduction of polar and flexible groups into the polymer backbone. The sulfonyl group has been known to meet this requirement¹²⁻¹⁹.

This paper describes the synthesis of new poly(silyl ether)s having chloromethyl and sulfonyl groups in their main chain. The structure and properties of the polymers were investigated by solubility, infra-red (i.r.) spectroscopy, nuclear magnetic resonance (n.m.r.), differential scanning calorimeter (d.s.c.) and X-ray diffraction (XRD). The effects of catalyst and solvent on the yields and molecular weights of the new poly(silyl ether)s are also discussed.

EXPERIMENTAL

Materials

Organic solvents were dried by using CaH₂ or Na metal and purified in the usual manner before use. The diglycidyl ether of bisphenol-S (bisphenol-S epoxy, BPSE) was prepared according to a method described elsewhere²⁰⁻²² and was recrystallized four times from the mixed solvents of ethanol and chloroform (4/1, v/v). Dichlorodiphenylsilane (CPS, supplied by Aldrich Chemical Co.) was purified by vacuum distillation; b.p. 173°C/10 mmHg (305°C/760 mmHg). Reagent grade triphenylphosphine (TPP), tetrabutylammonium chloride (TBAC), tetrabutylammonium bromide (TBAB),

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tetrabutylammonium fluoride (TBAF), tetrabutylphosphonium chloride (TBPC) and tetrabutylphosphonium bromide (TBPB) were used without further purification.

Polymerization

A typical procedure for the polyaddition of CPS with BPSE to produce poly(silyl ether) was as follows: CPS (0.38 g, 1.5 mmol), BPSE (0.54 g, 1.5 mmol), TBAB (0.048 g, 0.15 mmol) and toluene (2 ml) were charged into an ampoule. The gas from an ampoule that contained the monomer, solvent and catalyst was removed several times in a high-vacuum system. The addition reaction of CPS with BPSE was carried out at 50°C in the sealed ampoule for 24 h. Scheme 1 illustrates the synthesis.

The reaction mixture was diluted by adding chloroform (10 ml) and was washed twice with a minimal amount of water; some of the chloroform were then evaporated. The concentrated polymer solution was poured into hexane, and the polymer was dried *in vacuo* at 50°C. The yield of poly(silyl ether) was 0.86 g (93%). The number-average molecular weight (\bar{M}_n) of the polymer determined from gel permeation chromatography (g.p.c.) was 1.22×10^4 (PDI = 1.80). I.r. (film): 3054 ($\nu_{\text{arom.C-H}}$), 2946 ($\nu_{\text{aliph.C-H}}$), 1254 ($\nu_{\text{C-O-C}}$), 1120 ($\nu_{\text{Si-O}}$), 767 cm^{-1} ($\nu_{\text{C-Cl}}$). ^1H n.m.r. (CDCl_3 , tetramethylsilane): $\delta = 3.54\text{--}3.80$ (m, 4H, CH_2Cl), 3.95–4.20 (m, 4H, C– CH_2 –O), 4.33–4.51 (m, 2H, O– CH), 6.57–7.89 ppm (m, 8H, aromatic protons). Anal. calc. for $\text{C}_{30}\text{H}_{28}\text{O}_{16}\text{SiCl}_2$: C, 58.54%; H, 4.55%. Found: C, 58.85%; H, 5.39%. The high content of hydrogen may be due to the fact that the polymer was contaminated by the catalyst.

Characterization

The i.r. spectra were measured in the range 4000–400 cm^{-1} for the polymers in KBr discs (Jasco IR-700 spectrometer). Elemental analyses of the polymers were also conducted (Perkin-Elmer 2400 instrument). The glass transition temperature (T_g) was measured with a Du Pont 9000 differential scanning calorimeter at a heating rate 10°C min^{-1} , under a nitrogen atmosphere. Number-average molecular weight (\bar{M}_n) was determined by g.p.c. Four Waters (Ultrastragel) columns 300 \times 7.7 mm (10^2 , 10^3 , 10^4 and 10^5 Å in series) were used for g.p.c. analysis with tetrahydrofuran (THF) (1 ml min^{-1}) as the eluent. The eluents were monitored with an ultraviolet detector (Gilson model 116) at 254 nm; polystyrene was used as the standard. XRD was recorded by the powder method (Philips X-ray diffractometer, model PW 1710). The ^1H n.m.r. spectrum was recorded on a Jeol EX-400 instrument.

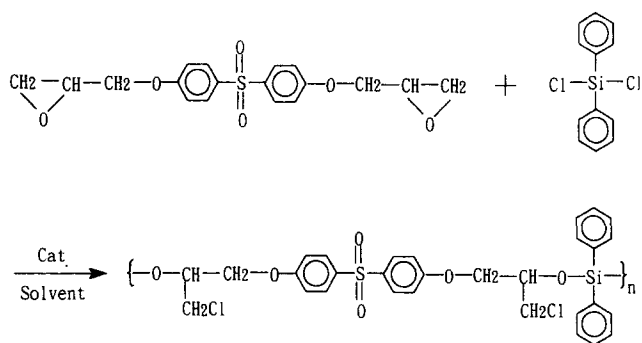
RESULTS AND DISCUSSION

The structure and properties of the polymers were investigated by solubility, i.r. spectrometer, ^1H n.m.r., d.s.c. and XRD. The polymer was soluble in chlorinated aliphatic hydrocarbons such as CH_2Cl_2 and CHCl_3 , aprotic solvents such as *N,N*-dimethylacetamide (DMAc) and dimethylformamide (DMF), aromatic solvents such as anisole and toluene, and other common organic solvents such as acetone, ethyl acetate, THF and acetonitrile, but insoluble in aliphatic hydrocarbons and alcoholic solvents.

Figure 1 shows the i.r. spectra of an epoxy based on

bisphenol-S and the corresponding poly(silyl ether). According to Figure 1, the epoxy ring absorption peak at 912 cm^{-1} completely disappeared and the absorption of the new Si–O linkages peak at 1120 cm^{-1} emerged after the addition reaction. Such an emergence suggests that the addition reaction had occurred and the poly(silyl ether) was obtained.

Table 1 summarizes the results of polyaddition of CPS and BPSE in various solvents by using TBAB as phase transfer catalyst. From this table, we can infer that poly(silyl ether)s with relatively high molecular weights were obtained, when the reactions were carried out in aromatic solvents such as toluene, anisole and chlorobenzene. Number-average molecular weights (\bar{M}_n) of the poly(silyl ether)s prepared in polar solvents such as 1-methyl-2-pyrrolidinone (NMP), DMF, DMAc and THF were slightly lower than those of the polymer



Scheme 1 Synthesis of poly(silyl ether)

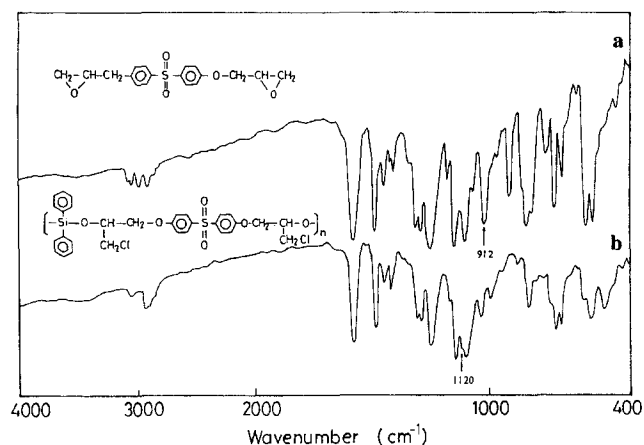


Figure 1 I.r. spectra of epoxy based on bisphenol-S and the corresponding poly(silyl ether): (a) epoxy based on bisphenol-S; (b) poly(silyl ether)

Table 1 Polyaddition of BPSE with CPS in various solvents^a

Run no.	Solvent	Yield (%)	$\bar{M}_n \times 10^{-4b}$	PDI ^b
1	Toluene	93	1.22	1.80
2	Anisole	92	1.39	1.23
3	Chlorobenzene	85	1.04	1.26
4	NMP	64	0.81	1.09
5	DMF	62	0.78	1.08
6	DMAc	64	0.87	1.07
7	THF	71	0.87	1.19

^a The reactions were carried out with 1.5 mmol of BPSE and 1.5 mmol of CPS in toluene (2 ml) using TBAB (0.15 mmol) as a catalyst at 50°C for 24 h

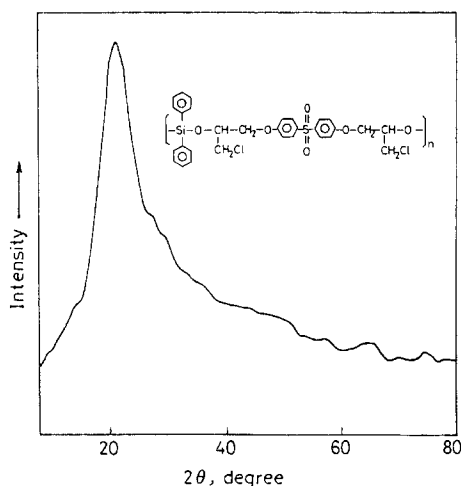
^b Estimated by g.p.c. based on polystyrene standards

Table 2 Polyaddition of BPSE with CPS using various catalysts^a

Run no.	Catalyst	Yield (%)	$\bar{M}_n \times 10^{-4b}$	PDI ^b
1	None	0	—	—
2	TPP	52	0.71	1.19
3	TBAC	77	1.01	1.11
4	TBAB	93	1.22	1.80
5	TBAF	84	1.30	1.26
6	TBPC	86	1.33	1.23
7	TBPB	60	.079	1.20

^a The reactions were carried out with 1.5 mmol of BPSE and 1.5 mmol of CPS in toluene (2 ml) using the catalyst (0.15 mmol) at 50°C for 24 h

^b Estimated by g.p.c. based on polystyrene standards

**Figure 2** XRD pattern of poly(silyl ether)

obtained in the aromatic solvents. This phenomenon may be accounted for by the fact that trace water in the polar solvents, which could not be completely removed, caused the hydrolysis of the dichlorosilane compound CPS and the unfavourable result for number-average molecular weight¹¹.

Table 2 presents the effects of catalysts on the yields and molecular weights of poly(silyl ether). This table reveals that the polyaddition of CPS with BPSE did not occur without a catalyst in a sealed ampoule at 50°C for 24 h. On the other hand, poly(silyl ether) with relatively low molecular weight ($\bar{M}_n = 7100$) was obtained in 52% yield under the same conditions when TPP was used as the catalyst. Poly(silyl ether)s with relatively high molecular weights ($\bar{M}_n = 7900$ –13 300) were prepared in 60–93% yields under the same reaction conditions, when TBAC, TBAB, TBAF, TBPC or TBPB was used as catalyst. These results demonstrate that (a) the polyaddition of CPS with BPSE proceeded quite smoothly when TPP were used as catalyst and (b) quaternary onium salts were used as catalysts under mild reaction conditions and that quaternary onium salts such as TBAB, TBAF and TBPC also have extremely high catalytic activity.

The poly(silyl ether) based on bisphenol-S with $\bar{M}_n = 12\,200$ has a glass transition temperature (T_g) of 68°C. Figure 2 displays the XRD pattern for poly(silyl ether) in terms of intensity versus 2θ where θ is the angle of diffraction (Bragg angle). The X-ray measurement indicated that the polymer is semi-crystalline.

CONCLUSIONS

A new poly(silyl ether) with a sulfonyl group and reactive pendant chloromethyl groups was successfully synthesized by the addition reaction of CPS with the diglycidyl ether of bisphenol-S (BPSE); the polymer's structure was confirmed spectroscopically. The polyaddition of CPS with BPSE proceeded very smoothly in toluene catalysed by quaternary ammonium or phosphonium salts, but did not occur without a catalyst under the same reaction conditions. Number-average molecular weights (\bar{M}_n) of the poly(silyl ether)s prepared in aromatic solvents were higher than those of the polymers obtained in polar solvents. Also, the poly(silyl ether) based on bisphenol-S with $\bar{M}_n = 12\,200$ was semi-crystalline and had a glass transition temperature (T_g) of 68°C. Experimental results indicated that the subsequent poly(silyl ether) with reactive pendant chloromethyl groups exhibited excellent solubility in common organic solvents.

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