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SILOXANE COPOLYMERS
CONTAINING CROWN ETHERS

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ABSTRACT

Functional siloxane copolymers containing crown ethers were synthesized through the polycondensation reaction of α,ω–hydroxypropylsiloxane oligomers with bis-(4'-chloroformyl)-dibenzo-18-crown-6, in solution. The compounds were characterized using IR, ^{1}H-NMR spectrophotometry and by elemental C, H, and Si analysis. All data agree with the proposed structures.

INTRODUCTION

Organofunctional polysiloxanes are a relatively new class of polysiloxanes copolymers that combines the unique properties of polydimethylsiloxanes with the reactivities of a wide range of organic groups [1]. Such linear organosiloxane oligomers may be used to obtain copolysiloxanes containing organic segments with specific properties in the backbone [2].

Crown ethers have received much attention because of their specific ability to form complexes with metal and organic cations and even neutral molecules [3,4]. They have opened the possibility for creating model compounds used in ion transportation through membranes, in molecular complexation and in catalyzing phase transfer processes [5]. Inserting crown ethers in a siloxane polymer support led to liquid extractants [6] and polymeric liquid crystals [7].

In order to synthesize polysiloxanes with macrocycles in the backbone we prepared a functionalized macrocycle through aromatic electrophilic substitution. The resulting product was subsequently used in a polycondensation reaction with oligosiloxanes having hydroxy-organofunctional endings.

The paper presents the synthesis of some new poly(siloxane-crown ether) copolymers containing α,ω–hydroxypropyl-polydimethylsiloxane as the inorganic unit and a macrocycle combination such as bis-(4,4'-dicarboxy)-dibenzo-18-crown-6.

EXPERIMENTAL

Materials

1,3-Bis(3-hydroxypropyl)-1,1,3,3-tetramethyldisiloxane (used in the equilibration reaction) was supplied by Petrarch Systems Inc.

Octamethylcyclotetrasiloxane was purchased from Fluka. Methylene chloride was dried and distilled over P_2O_5 before use.

Pyridine was dried over KOH for 24 H and then freshly distilled before use under a dried nitrogen atmosphere.

4,4'-dicarboxy-dibenzo-18-crown-6 was obtained and purified according to [8].

Tetrabutylammonium hydroxide solution 0.1 N was supplied by Fluka.

Apparatus

IR spectra were recorded on a Specord M80 spectrophotometer using KBr pellets.

UV spectral data were obtained using a Specord M42 spectrophotometer.

^{1}H-NMR Spectra were registered using a JEOL C-80 HL spectrophotometer and TMS as internal standard.

The molecular weight of the acid chloride was obtained by chlorine titration with 0.1 N tetrabutylammonium hydroxide solution in isopropyl alcohol.

Numerical molecular weight of the α,ω-hydroxypropyl-polydimethylsiloxane oligomers was determined from the ^{1}H-NMR spectra.

The inherent viscosities of the copolymers in toluene at 20°C were obtained with a Canon-Ubbelohde viscometer.

Synthesis of 2,3,11,12-bis-(chloroformyl)-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene or bis-(4-chloroformyl)-dibenzo-18-crown-6 (I).

An amount of 1.2 g (2.69 mmol) diacid was charged under a dry nitrogen atmosphere to a round-bottom flask fitted with a reflux condenser. 0.97 g (4 mmol; 0.6 mL) $SOCl_2$ were added and the reaction mixture was refluxed until the diacid passed into solution. A catalytical amount of DMF was dropped into the reaction mixture and refluxing was continued for 20 hours. Excess $SOCl_2$ was distilled off and the dichloride was recovered as a yellowish solid weighing 1.1 g (yield 91.3%). The product was used without further purification. The IR spectrum showed the displacement of the carbonyl bond absorbance band from 1700 cm^{-1} in the diacid to 1780 cm^{-1} in the acid's dichloride.

Synthesis of hydroxypropyl terminated polydimethylsiloxane oligomers [9] (II).

The synthesis of α,ω-bis(3-hydroxypropyl)polydimethylsiloxanes was performed through cationic ring-opening polymerization of octamethylcyclotetrasiloxanes in the presence of 1,3-bis(3-hydroxypropyl)tetramethyldisiloxane and a styrene-divinylbenzene ion exchanger with sulfonic acid groups (VIONIT CS 34C) as catalyst. The reaction mixture was stirred for 36 hours at 80°C, cooled to room temperature and filtered. The cyclic siloxanes were distilled at 120°C (10 mm Hg) yielding a clear thick oil.

Synthesis of siloxane-crown ethers copolymers (III).

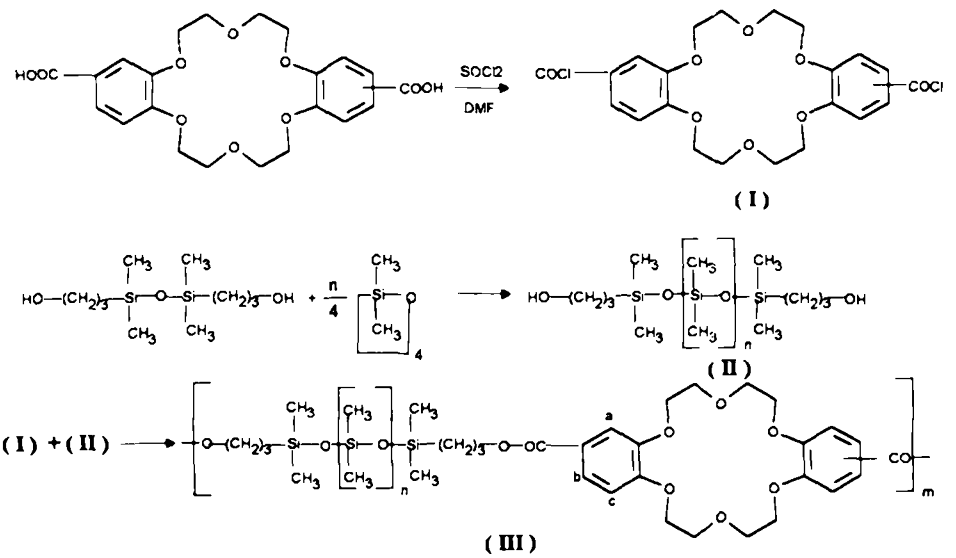
A polysiloxane : crown ether derivative molar ratio of 1:1 was employed. The reaction was carried out in refluxing methylene chloride in the presence of pyridine as hydrochloric acid acceptor. After pyridine hydrochloride has been filtered off, distillation of the solvent led to viscous or crystalline polycondensation products.

RESULTS AND DISCUSSION

Siloxane-crown ether copolymers were synthesized through a polycondensation reaction in solution (Scheme 1). Bis-(4-chloroformyl)-dibenzo-18-crown-6 was obtained by the reaction of the corresponding diacid with $SOCl_2$ and in the presence of DMF as catalyst.

α,ω-Hydroxypropylsiloxanes with molecular weights of 251 (1), 1000 (2), and 3000 (3) respectively, were synthesized using bulk equilibration technique of octamethylcyclotetrasiloxane with bis(α,ω-hydroxypropyl)disiloxane at calculated molar ratios of comonomers. The expected molecular weights were similar to those obtained from ^{1}H-NMR data.

The IR spectra (Table 1) of the synthesized products show absorption bands that are in agreement with the expected polymeric structure [10].



Scheme 1

The Si-O-Si bond absorbance around 1020 cm^{-1} and the displacement of the carbonyl bond absorbance from 1780 cm^{-1} to 1720 cm^{-1} confirm the fact that polycondensation reaction took place.

A 0.01% solution of the synthesized copolymers in methylene chloride was used for recording UV spectra. According to the data presented in Table II, all copolymers absorb at the same wavelength but the absorbance values decrease with the increasing molecular weight of the siloxane oligomers. In comparison with the IR spectra these data allow us to conclude that the contribution from the organic unit becomes smaller when the molecular weight of the siloxane oligomer used in synthesis is raised.

The molecular weight estimation for the oligomers was accomplished by measuring the integrated signals for the peak at δ, 0.15 ppm [10]: 12 H, s, disiloxane; 60 H, s, oligomer M_w= 1000; 232 H, s, oligomer M_w= 3000.

For other protons all oligomers displayed the same ^{1}H-NMR spectra: δ, ppm: 0.55 (-Si-$\underline{CH_2}$, 4H, m); 1.65 (-Si-CH_2-$\underline{CH_2}$-, 4H, m); 3.56 (-Si-$(CH_2)_2$-$\underline{CH_2}$-OH, 4H, m).

Table I

Infrared Absorptions [10]

Absorption (cm^{-1})			Assignment
Copolymer (1)	(2)	(3)	
3060 (w)	3000 (w)	3000 (w)	CH (phenyl)
3050 (w)	3070 (w)	3050 (m)	
2980 (m)	2980 (m)	2970 (m)	CH
2865 (w)	2860 (w)	2860 (w)	
1730 (s)	1730 (s)	1720 (m)	C=O
1600 (m)	1580 (m)	1580 (m)	C=C
1450 (m)	1455 (m)	1450 (m)	
1230 (w)	1240 (m)	1240 (m)	$Si-CH_3$
1260 (s)	1265 (s)	1270 (s)	$C-O-C_{ar}$
1060 (s)	1090 (s)	1060 (s)	C-O-C
1020 (s)	1050 (s)	1020 (s)	Si-O
800 (m)	805 (m)	800 (m)	$Si-CH_3$

Table II

UV Spectral Data

Molecular weight	251	1000	3000
Wavelength (cm^{-1})	Absorbance values for the copolymers		
292.5	0.29	0.14	0.04
259	0.55	0.22	0.09

Table III

C,H, and Si Elemental Analysis of Copolymers

No.	C (%)		H (%)		Si (%)	
	calc.	found	calc.	found	calc.	found
1.	57.96	58.01	6.94	6.89	8.45	8.51
2.	45.91	45.86	7.49	7.41	22.32	22.60
3.	37.40	37.48	7.88	7.93	32.11	32.31

In the case of the prepared copolymers the following supplementary chemical shifts were registered: δ, ppm: 3.95-4.13 (-O-CH_2-CH_2-O-, 16H, m); 6.88 (Hc, 2H, d); 7.50 (Ha, 2H, d); 7.65 (Hb, 2H, m).

Spectral analysis reveals that no side reactions occur. The polycondensation process follows a normal course, exibiting only slight differences concerning yields and reaction times, all these as a consequnce of the increasing molecular weights of all the β-hydroxypropyl-oligomers.

The reaction mixture remained homogeneous during the polycondensation reaction time.

Viscous or solid white products were obtained with a 80-90% polymerization yield. Intrinsic viscosity values were within 0.42-0.45 dL/g (measured in DMF at 25°C).

Copolymers elemental analysis data are presented in Table III.

These copolymers are soluble in most common organic solvents such as tetrahydrofuran, chloroform, pyridine, DMF, DMSO, and N,N-dimethylacetamide.

Transparent and flexible film can be cast from solution.

Future investigation will be made to obtain some other physical characteristics of these new compounds.

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