Siloxane oligomer diols as potential intermediates for novel durable coatings

J Kozakiewicz

Industrial Chemistry Research Institute, 01-793 Warsaw, ul.Rydygiera 8, Poland

Introduction

Siloxane oligomer diols known also as silicone oligomer diols or polysiloxane diols are hydroxyalkyl-terminated oligomeric linear siloxanes of general Structure 1

\[
\text{R}_1 \quad \text{R}_3 \quad \text{R}_4
\]

\[
\text{HO} - \text{R} - \text{Si} - \text{O} - (\text{Si} - \text{O})_x - \text{Si} - \text{R} - \text{OH}
\]

Structure 1

where:

- \text{R} = \text{alkylene}
- \text{R}_1, \text{R}_2, \text{R}_3, \text{R}_4 = \text{alkyls or phenyls.}

They react with isocyanates in the same way as normal polyether- or polyester-diols, forming hydroxyl-terminated segmented poly(siloxaneurethanes) or NCO-terminated poly(siloxaneurethane) prepolymers depending on the NCO/OH ratio. Because of the presence of polysiloxane blocks, considerable improvement of certain properties (eg low temperature flexibility, high temperature resistance or ageing resistance) of poly(siloxaneurethanes) can be expected as compared with standard polyurethanes. The unique surface properties of poly(siloxaneurethanes) resulting from surface enrichment with siloxane segments are also very important as far as coating applications are concerned.

Several manufacturers are now offering siloxane oligomer diols of Structure 1 with a good choice of ‘x’ and ‘R’ and \(\text{R}_1=\text{R}_2=\text{R}_3=\text{Me}.\)

Siloxane oligomer diols that contain two OH groups at one end of the siloxane chain (see Structure 2) have been described in the literature. They can be synthesized by hydrolysis of the corresponding poly(dimethylsiloxane) containing a silane end group with 3-allyloxy-1,2-propanediol.

\[
\text{R} - \text{Si} - (\text{O} - \text{Si} - )_x - \text{R} - \text{OH} - \text{CH}_2\text{OH}
\]

Structure 2

where \(\text{R} = \text{alkylene}\)

In the reaction with diisocyanates, such ‘pseudo-siloxane oligomer diols’ form ‘pseudo-(poly)urethanes’ with pendant siloxane chains which impart certain specific properties to them. Thus, enhanced hydrophobicity can be expected as compared to ‘normal’ poly(siloxaneurethanes). Their other advantage is that some functional groups (eg allyl) can be bonded to the end of pendant siloxane chains enabling easy crosslinking. Based on this concept, interesting UV-curable or other radically polymerizable systems have been developed.

Siloxane macromonomers capable of polymerization or copolymerization can also be obtained from ‘normal’ siloxane oligomer diols either directly by reaction with isocyanates containing unsaturated units or from siloxane oligomer dio-based, NCO-terminated poly(siloxaneurethane) prepolymers and hydroxyalkyl(meth)acrylates. Such ‘macromonomers’ are potential intermediates for coatings.
The possibility of introducing the functional groups or other blocks imparting specific properties to poly(siloxaneurethanes) directly to the siloxane oligomer diol chain has attracted several investigators. Synthesis of siloxane oligomer diols with quaternary ammonium salt groups has been patented recently and described in the literature. The process comprises cohydroisilylation of allylic derivatives (N,N-dimethylallylamine and allyloxytrimethylsilylane) with various poly(dimethylsiloxane-hydrogenmethylsiloxanes) and subsequent quaternization of the N-allyl groups combined with unblocking of alcoholic functions. Such modified siloxane oligomer diols impart biocidal properties to poly(siloxaneurethanes) synthesized from them. The synthesis of fluorine-containing siloxane oligomer diols (and other α, α-bifunctional siloxane oligomers) has been also developed recently.

Especially interesting from the coating application point of view seems to be the method of introducing polyether blocks to siloxane oligomer diols, as recently patented by BASE. The starting materials are poly(tetramethylene glycol) or other polyetherdiol diallyl ether and methylhydrogen siloxane. After hydrosilylation, a Si-H – terminated poly(ethersiloxane) is formed which is then again reacted with H₂SiOCH₂-GH=CH₂. After subsequent hydrolysis, the product of Structure 3 is obtained:

It is a linear diol containing both siloxane and polyether blocks in the main chain. These are interesting intermediates for poly(siloxaneurethanes). In such poly(siloxaneurethanes), much better siloxane and polyether segment compatibility can be expected that in the reaction products of diisocyanate with the blend of siloxane oligomer diol and polyetherdiol or of poly(siloxaneurethane) prepolymer with polyetherdiol.

The use of polyethersiloxanediol in synthesis of poly(siloxaneurethanes) applied as coatings has not yet been reported but it is obvious that it is a very promising intermediate for this purpose.

Poly(siloxaneurethanes) used so far in coating applications were synthesized mostly from siloxane oligomer diols of Structure 1. A review of these applications has been presented. These applications include:

- water-repellent coatings on various substrates
- anti-friction and wear-resistant coating binders for magnetic and thermal recording media
- antithrombogenic coatings
- antifouling coatings.

The recently reported (mostly in the patent literature) coating applications of poly(siloxaneurethanes) fit roughly to this list.

The study presented below concentrated on utilizing various commercially available siloxane oligomer diols of Structure 1 as intermediates for moisture-curable and water-dispersible poly(siloxaneurethanes) that could be useful as coatings.

**Experimental**

**Moisture-curable poly(siloxaneurethanes)**

Siloxane oligomer diols (SOD) of Structure 1 were used in the synthesis of moisture-curable poly(siloxaneurethanes) (MCPSUR):

- SOD-1: R = -(CH₂)₅ - O- (CH₂)₂ - ; x = 20
- SOD-2: R = -(CH₂)₅ - O- (CH₂)₂ - ; x = 40
- SOD-3: R = -(CH₂)₅ - O- (CH₂)₂ - ; x = 72
- SOD-4: R = -(CH₂)₅ - ; x = 8
- SOD-5: R = -(CH₂)₅ - ; x = 30

For all SOD R₁ = R₂ = R₃ = R₄ = -(CH₂)₅ -

All the SOD products were colourless liquids. This structures of the allylène groups – R – adjacent to –OH and x values, reported by the manufacturer, were proven by 1H NMR and 13C NMR, for SOD-4 and SOD-5, the results obtained from NMR were consistent with the manufacturer's data while for SOD-1, SOD-2 and SOD-3, the structures found from NMR did not correspond to the reported ones. 13C NMR spectra of SOD-1 and SOD-2 are presented in Figures 1 and 2.

MCPSUR were prepared by the reaction of SOD with a twice molar excess of isophorone diisocyanate (IPDI from Huls) according to the method described elsewhere and characterized by FTIR, GPC and 1H and 13C NMR. The viscosity (Brookfield) of MCPSUR and the NCO content (standard titration) were also determined. Moisture curing was performed at 25°C and at 50% R.H. The mechanical properties of the moisture-cured films were determined using standard methods.

**Water-dispersible poly(siloxaneurethanes)**

Water-dispersible, NCO-terminated PSUR prepolymers were prepared by the reaction of SOD and IPDI according to the process described in the literature for standard