Novel Urea-Siloxane Polymers as Gelling Agents for Silicone Fluids: Influence of the Hard Segment

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Summary. A series of polyureas were synthesized from amino terminated polydimethylsiloxane oligomers, diamine comonomers, and various diisocyanates. These polymers were characterized by nuclear magnetic resonance (NMR), infrared (IR) spectroscopy, and size exclusion chromatography (SEC). The gelation behavior in silicone fluids such as dimethylcyclosiloxanes was investigated. The influence of the structure of the hard segment on the gelation properties was evaluated.

Keywords. Siloxane; Polyurea; Urea-siloxane copolymers; Gelation behavior.

Introduction

Polydimethylsiloxane (*PDMS*) as low Tg-polymer is the basis for silicone elastomers. Here, the *PDMS* chains are chemically crosslinked and a permanent network exists. Therefore no further thermal forming of the final part is possible. If the crosslinks between the chains are of reversible nature like in thermoplastic elastomers, these elastomers can be processed from the melt [1, 2].

In thermoplastic silicone elastomers the soft segment is *PDMS* and the hard segment consists of moieties with either high melting temperatures or high glass transition temperatures. The type of the hard segment, the relative molecular weight of the soft segment, and the ratio of the hard and soft segments tailor the properties of the polymer. The hard segments can be crosslinked *via* hydrophobic interactions, liquid crystalline interactions, hydrogen bonding, or donor/acceptor interactions.

This paper describes the synthesis and properties of polymers containing dimethylsiloxane soft segments and urea hard segments. In order to establish structure/property

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relations, in particular with respect to the gelation behavior of low molecular weight silicone fluids, the chemical structure of the urea segment was varied. The influence of the soft segment is described elsewhere [3].

Results and Discussion

The main-chain urea-siloxane copolymers were synthesized according to the following Scheme.

The polymerization was carried out with *THF* as solvent at room temperature. It was found that this solvent leads to high molecular weight, which is in agreement with the synthesis of similar systems described in the literature [4]. A mixture of diisocyanates was slowly added to the solution of the siloxane diamine (Scheme 1a). Also diamine comonomers together with the siloxane diamine were used to increase the length of the hard segment. In this case the siloxane diamine and the diamine comonomer were added to the diisocyanate (Scheme 1b).

If the IR spectrum showed isocyanate groups, the polymer was dissolved in *THF*/diethylamine because free isocyanate groups can lead to crosslinked polymers at temperatures above 100°C. At elevated temperatures diisocyanate end groups can react with the urea linkage to allophanate structures [5].
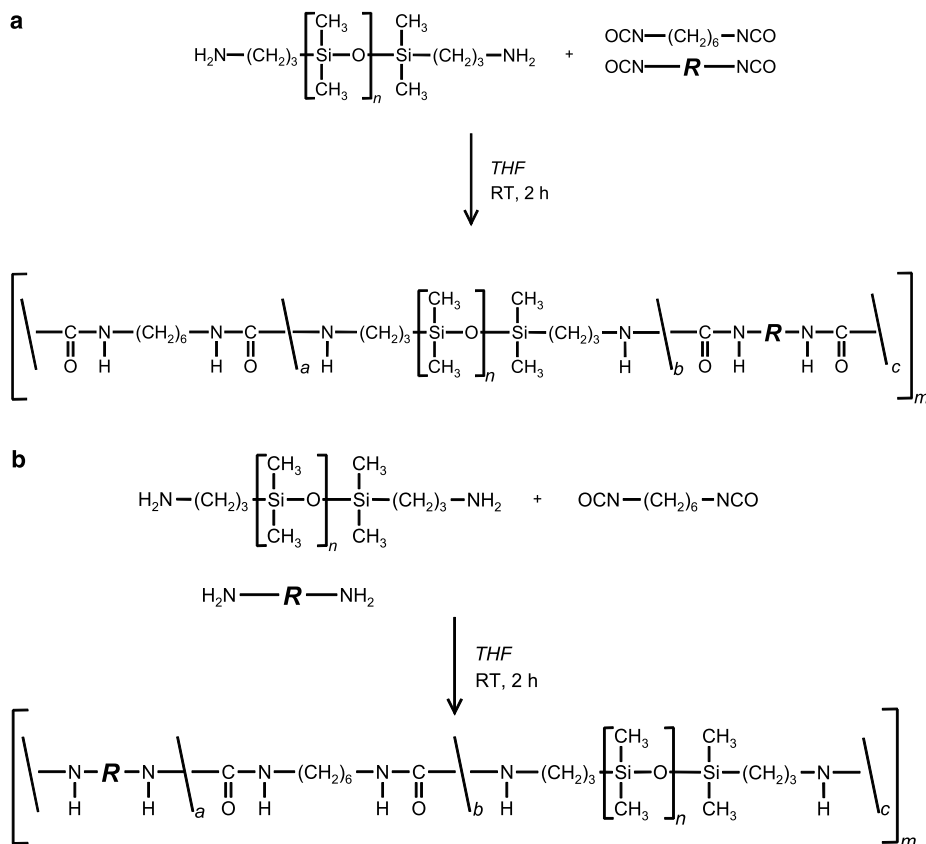
Scheme 1

The IR spectra of polymers show characteristic signals, such as the NH-peak at $3320\,\text{cm}^{-1}$ and the signals of the urea linkage appear at 1630 and $1577\,\text{cm}^{-1}$. No peak at $2270\,\text{cm}^{-1}$ indicates the absence of isocyanate endgroups.

With ^{1}H NMR spectroscopy the polymerization can also be confirmed. The signal at 2.6 ppm, which can be assigned to the methylene group next to the amino group in the telechelic diaminosiloxane, is no more visible. Instead a signal at 3.1 ppm appears, which is assigned to the same methylene group linked to the urea group.

Following polyureas were synthesized based on a siloxanediamine (*DMS-A15*) and a mixture of diisocyanates (hexamethylene diisocyanate/isophorone diisocyanate, and hexamethylene diisocyanate/2,2(4),4-trimethyl-1,6-diisocyanatohexane). The diisocyanates were selected according to former results [3]. Two series of polyurea were produced as shown in Tables 1 and 2.

These tables show the molecular weight of the copolymer. The synthesis of the copolymers with 2,2(4),4-trimethyl-1,6-diisocyanatohexane leads to polymers with lower molecular weight compared to the other polymers. The molecular weight is important for the gelation properties of the polymer because the polymer chain needs a certain amount of the hard segments for the thermoreversible crosslinking.

Thermoreversible silicone gels are of principal interest for several applications in cosmetics [6–10]. Therefore, polymers were tested with respect to the potential to gel silicone fluids such as cyclosilicones for example *DOW 245* that is used as ingredient in cosmetic formulations. This fluid consists of tetra-, penta-, and hexa-cylcodimethylsiloxane derivatives. As a general procedure for the preparation of

Table 1. Synthesized main-chain urea-siloxane copolymers based on isophorone and hexamethylene diisocyanate

Number	Molar ratio of hexamethylene diisocyanate and isophorone diisocyanate	Molecular weight $(M_n)/(\text{g/mol})^{\text{a}}$
1	1:0	78400
2	2:1	84500
3	1:2	81000
4	0:1	50090

[a] Determined by SEC with a polystyrene calibration

Table 2. Synthesized main-chain urea-siloxane copolymers based on hexamethylene diisocyanate and 2,2(4),4-diisocyanatohexane

Number	Molar ratio of hexamethylene diisocyanate and 2,2(4),4-trimethyl-1,6-diisocyanatohexane[a]	Molecular weight $(M_n)/(\text{g/mol})^{\text{b}}$
1	1:0	78400
5	4:1	38470
6	3:2	27200
7	2:3	34090
8	1:4	20460
9	0:1	75300

[a] 1:1 mixture of the isomers; [b] determined by SEC with a polystyrene calibration

the gels the polymer is heated in the silicone solvent until the polymer is comple-
tely dissolved. Then the solution was slowly cooled down and the solution becomes
hard if gelation occurs. Important for an application is also the visible appearance
of the gel. Particular interest is in clear gels. Visible observation, the falling ball
method, differential scanning calorimetry, and rheology are commonly used to
determine the gelation temperature [10–14]. In our study we used a visible obser-
vation. During the gelation the temperature was measured within the gel.

The concentration of the polymer, which was used for the comparison of gel
properties, is 20 *wt%* in *DOW 245*. The gelation temperatures of the polymers were
measured (Table 3, Fig. 1).

The gel point decreases if mixtures of diisocyanates were used. The bond strength
between the urea units is higher if both units have the same chemical structure.

Table 4 demonstrates this effect, too. Hexamethylene diisocyanate and 2,2(4),4-
trimethyl-1,6-diisocyanatohexane were used. The gel point decreases if hexa-
methylene units in the polymer were replaced by 2,2(4),4-trimethylhexane-1,6-diyl
units. From a molar ratio of 3 to 2 the polymer does not gel the solvent, the solution
becomes only viscous.

In further experiments the length of the hard segment was changed. Therefore
an additional diamine comonomer increases the length of the urea segment and

Table 3. Gel points of the copolymers with isophorone diisocyanate

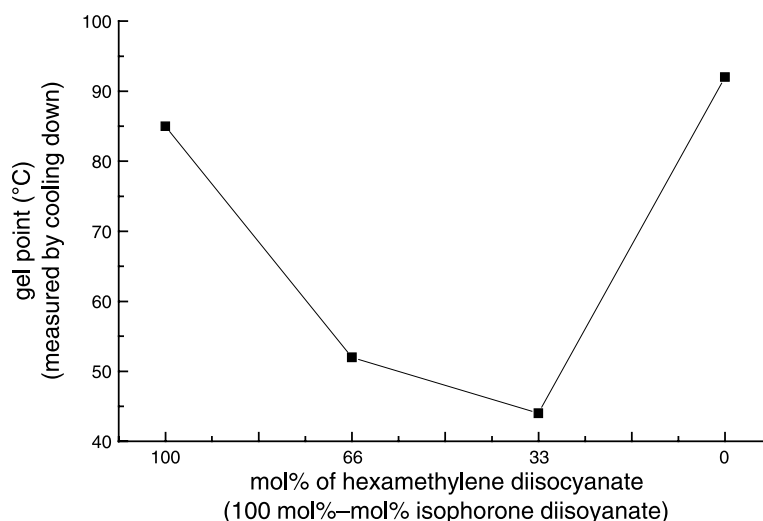| Molar ratio of hexamethylene diisocyanate and isophorone diisocyanate	Gel properties (20 *wt%* in *DOW 245*)
1:0 (**1**)	clear gel, gel point: 85°C
2:1 (**2**)	clear gel, gel point: 52°C
1:2 (**3**)	clear gel, gel point: 44°C
0:1 (**4**)	clear gel, gel point: 92°C

Fig. 1. Dependence of the gel point on the ratio of hexamethylene and isophorone units in the polymers

Table 4. Gel points of the polymers with 2,2(4),4-trimethyl-1,6-diisocyanatohexane

Molar ratio of hexamethylene diisocyanate and 2,2(4),4-trimethyl-1,6-diisocyanatohexane	Gel properties (20 wt% in DOW 245)
1:0 (**1**)	clear gel, gel point: 85°C
4:1 (**5**)	clear gel, gel point: 50°C
3:2 (**6**)	clear gel, gel point: 25°C
2:3 (**7**)	clear highly viscous solution
1:4 (**8**)	clear highly viscous solution
0:1 (**9**)	clear highly viscous solution

Table 5. Synthesized main-chain urea-siloxane copolymers based on siloxane diamine and diamine comonomers

Diamine comonomer	Molar ratio of non-siloxane diamine and siloxane diamine	Molecular weight (M_n)/(g/mol)[b]
R = tetramethylene (**10**)	1:4	insoluble
R = 1,3-phenylene (**11**)	1:4	18050
R = 2,2,4-trimethylhexane-1,6-diyl and 2,4,4-trimethylhexane-1,6-diyl[a] (**12**)	1:4	23790
R = 2,2,4-trimethylhexane-1,6-diyl and 2,4,4-trimethylhexane-1,6-diyl[a] (**13**)	1:3	16000

[a] 1:1 mixture of the isomers; [b] determined by SEC with a polystyrene calibration

consequently increases the interactions and the gel point. The following diamine comonomers were used together with the siloxane diamine (Table 5).

The table demonstrates that the molecular weight of the polymers is lower compared to the polymers without a diamine comonomer. But the gel point increases because the urea unit was extended. The polymer with 1,4-diaminobutane is not soluble in *DOW 245*. No gel point can be determined. The polymer with 1,3-diaminobenzene can gel the silicone solvent, but the gel is yellow colored. The polymers with 2,2(4),4-trimethyl-1,6-diaminohexane lead to clear and colorless gels. These polymers are less elastic compared to the polymers without the diamine comonomer (Table 6).
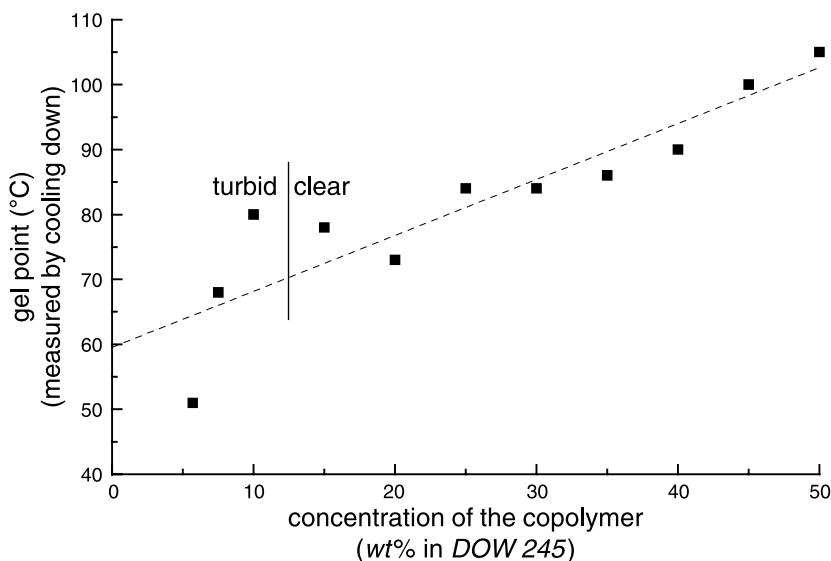
The dependence of polymer (**13**) concentration on the gel point was also investigated because the properties of this polymer are suitable for cosmetic formulations (Table 7, Fig. 2).

Table 6. Gel points of the polymers with diamine comonomers

Number	Gel properties (20 wt% in DOW 245)
10	not soluble
11	clear yellow gel, gel point: 93°C
12	clear gel, gel point: 78°C
13	clear gel, gel point: 73°C

Table 7. Gel point depending on the concentration of polymer **13**

Concentration of **13** in *DOW 245*/wt%	50	45	40	35	30	25	20	15	10	7.5	5
gel point/°C	105	100	90	86	84	84	73	78	80	68	51

Fig. 2. Dependence of the gel point on the concentration of polymer **13** in *DOW 245*

It can be observed that the gel point increases as expected with increasing polymer content. Another interesting observation is that the gel is turbid if the concentration of polymer **13** in *DOW 245* is below 15 *wt*%. The polymer does not form a network over the entire gel. The resulting gel is heterogeneous and consists of gel particles and free solvent. This leads to a turbid gel because the light was refracted at the interfaces.

It was demonstrated that main-chain urea-siloxane copolymers are able to form gels in silicone solvents. The gel properties (gel point and optical properties) depend strongly on the structure of the polymer but can be tailored on a wide temperature range. The hard segment is important for the dissolution of the polymer in the silicone solvent. If the hydrogen bonds of the urea unit are disordered the gel point decreases and no gel is formed. The strength of the bonds in the hard segment is responsible for the solubility or the insolubility in the solvent.

Experimental

Hexamethylene diisocyanate, 2,2(4),4-trimethyl-1,6-diisocyanatehexane (1:1 mixture of the isomers), isophorone diisocyanate, 1,4-diaminobutane, phenylenediamine and 2,2(4),4-trimethyl-1,6-diamino-hexane (1:1 mixture of the isomers) were purchased from Aldrich (München, Germany) and were used without further purification. The siloxanediamine (*DMS-A15*; equivalent molecular weight: 2500 g/mol) was supplied by Gelest (Karlsruhe, Germany) and used without further purification. The

silicone solvent (*DOW 245*) was supplied by DOW (Arlington, USA). *THF* was distilled over metallic potassium before using. All other chemicals were used as received.

All reactions were carried out in a two-necked flask with a dropping funnel. The mixture of the diamines or diisocyanates was dissolved in dry *THF*. The reaction was carried out by the slow addition of the diisocyanate or siloxanediamine (stoichiometric ratio of the diisocyanate and the diamine) at room temperature *via* dropping funnel.

After 2 h the solvent was distilled off. If the resulting polymer had isocyanate endgroups (IR spectroscopy: 2270 cm^{-1}), the polymer was dissolved in *THF*/diethylamine, stirred for 1 h, and isolated by removing the solvent. The obtained polymer was directly used for the characterization.

IR spectra were collected using a Biorad/Digilab FTS 40 spectrometer (München, Germany). Samples were coated on NaCl plates for measurement. All NMR spectra were acquired on a Bruker Avance 250 spectrometer (Rheinstetten, Germany) operating at 250 MHz for ^{1}H and at 62.5 MHz for ^{13}C acquisition. CDCl$_3$ obtained from Aldrich was used as solvent. Molecular weight was determined by SEC using a calibration with polystyrene (*PS*) standards from Polymer Standards Services (PSS, Mainz, Germany). The equipment consisted of a Waters (Milford, USA) pump 510 and four columns (PSS, Mainz, Germany) (SDV-Gel (5μ): 105, 104, 103, 102 A). The solvent was *THF*. The polymers were detected by a refractive index detector. The molecular weight average (M_n: number average of molecular weight) as given in Results and Discussion was calculated according to the *PS* calibration. The polydimethylsiloxane segments have low specific refractive increments (dn/dc) in *THF* solution, therefore higher concentrations (up to 5 mg/cm^3) were used to enlarge the signal.

Acknowledgements

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