Novel Urea-Siloxane Polymers as Gelling Agents for Silicone Fluids

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Summary: A series of polyureas were synthesized from amino terminated polydimethylsiloxane oligomers of different molecular weight and various diisocyanates. These polymers were characterized by nuclear magnetic resonance (NMR), infrared (IR) spectroscopy and size exclusion chromatography (SEC). The formation of hydrogen bonding of the urea segments was investigated by temperature dependent IR-spectroscopy. The gelation behavior in silicone fluids such as dimethylcyclosiloxanes was investigated. The influence of the structure of the hard and the soft segment on the gelation properties was evaluated.

Introduction

Polysiloxanes such as polydimethylsiloxane (PDMS) combine several unique properties. They have a low glass transition temperature, high thermal and oxidative stability, high UV-resistance, low surface energy and a strong hydrophobicity, high permeability to many gases and good electrical properties. These properties are independent over a wide temperature range. This spectrum of properties opened the application of polysiloxanes as materials in medical and cosmetic applications.[1-3]

PDMS as low Tg-polymer is the basis for silicone elastomers. Here, the PDMS chains are chemically crosslinked and a permanent network is formed. After the crosslinking step no further thermal forming of the final part is possible. However in thermoplastic elastomers the crosslinks between the chains are of reversible nature allowing processing from the melt. [4,5]

A controlled synthesis of AB, ABA or $(AB)_n$ block or segmented copolymers is one way to obtain thermoplastic elastomers. 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 and nature of the hard segment, the relative

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molecular weight of the soft segment and the ratio of the hard and soft segments are the main parameters to influence and tailor the properties. The interaction of the hard segments, which is responsible for the reversible crosslinking, can be a result of 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 relations, in particular with respect to the gelation behavior of low molecular weight silicone fluids, on one hand the length of the siloxane segment and on the other hand the chemical structure of the urea segment were varied.

Experimental

The diisocyanates were purchased from Aldrich (München, Germany) and used without further purification. The siloxane diamines with different molecular weight were purchased from Gelest (Karlsruhe, Germany) (DMS-A12, DMS-A15, DMS-A21 and DMS-A27) and Goldschmidt (Essen, Germany) (A2120) and also used without further purification. The silicone solvent (DOW 245) was supplied by DOW Corning (Arlington, USA). Tetrahydrofurane (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 siloxane diamine was dissolved in dry THF. The reaction was carried out by the slow addition of the diisocyanate (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/diethyl amine, stirred for 1 h and isolated by removing the solvent. The obtained polymer was directly used for the characterization.

IR Spectroscopy: IR spectra were collected using a Biorad/Digilab FTS 40 spectrometer (München, Germany). Samples were coated on NaCl plates for measurement.

NMR Spectroscopy: All NMR spectra were acquired on a Bruker Avance 250 spectrometer (Rheinstetten, Germany) operating at 250 MHz for ^{1}H and 62.5 MHz ^{13}C acquisition. $CDCl_3$ obtained from Aldrich was used as solvent.

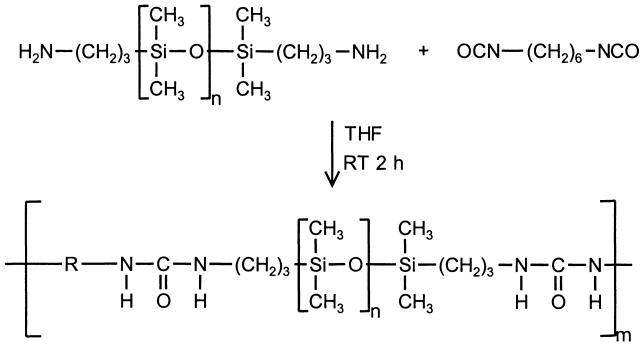
Size Exclusion Chromatography: Molecular weight was determined by SEC using a calibration with polystyrene (PS) standards from Polymer Standards Services (PSS, Mainz; Germany). The equipment consisted of a Waters (Milford, USA) pump 510 and four columns (PSS, Mainz, Germany) (SDV-Gel (5µ): 10^5, 10^4, 10^3, 10^2 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 (until 5 mg/ml) were used to enlarge the signal.

Results and Discussion

Synthesis and properties of polymers with different length of siloxane segment

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.[6] The diisocyanate was slowly added to the solution of the siloxane diamine. If the IR spectrum shows isocyanate groups, the polymer was dissolved in THF/diethyl amine because free isocyanates groups can lead to crosslinked polymer at temperatures above 100 °C. At elevated temperatures diisocyanate end groups can react with the urea linkage to form allophanate structures.[7] Table 1 lists the molecular weight of the used telechelic diamino siloxanes and the synthesized polymers with hexamethylene diisocyanate.

Table 1. Synthesized main-chain urea-siloxane polymers based on different siloxane diamines and hexamethylene diisocyanate.

Number	Siloxane diamine	Urea-siloxane polymer	
	molecular weight (M_n) (g/mol)	molecular weight (M_n) (g/mol)	properties
A1	900[a]/800[b]	50100[c]	clear colorless elastic solid
A2	2500[a]/2600[b]	87000[c]	clear colorless elastic solid
A3	5000[a]/5200[b]	104800[c]	clear colorless wax
A4	27000[a]/-[d]	107600[c]	clear colorless highly viscous liquid

a) given by the supplier.
b) measured by endgroup analysis based on ^{1}H-NMR.
c) determined by SEC with a polystyrene calibration.
d) The concentration of the endgroups of DMS-A32 is too low for the detection by ^{1}H-NMR.

The molar concentration of the hard segments decrease with a higher molecular weight of the soft segment. This effect leads to pronounced changes of the appearance of the polymer. Polymers A1 and A2 are colorless elastic solids, A3 is a clear colorless wax and A4 is a highly colorless viscous liquid.

The IR-spectra of polymers (cf. Figure 1) show characteristic signals, such as the NH-peak at 3320 cm^{-1} and the signals of the urea linkage appear at 1630 cm^{-1} and 1577 cm^{-1}. No peak at 2270 cm^{-1} indicates the absence of isocyanate endgroups. The wavenumber and intensity of the absorption of these peaks depends on the temperature. From low molecular model substances it is known that the absorption can be attributed to different environments of the carbonyl group.[8] These experiments were made with ethylene diphenylurea and 2-methylpentane-1,5-diphenylurea.

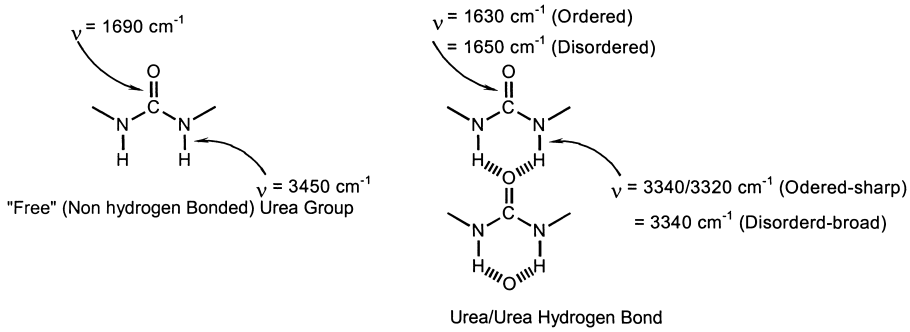


Figure 1. Wavenumber of the absorption of urea units in free and hydrogen-bonded form.[8]

Temperature dependent IR-spectra of A2 are shown in Figure 2. The figure illustrates the changes of the maximum of the absorption of the carbonyl peak (at 1630 cm^{-1}) (top) and the N-H vibration (at 3340 cm^{-1}) (bottom). For the carbonyl peak it can be seen that the maximum is shifted to higher wavenumbers and the relative intensity changes, too. The strongest change is between 30 °C and 90 °C. In this range a shift of the maximum absorption from 1625 cm^{-1} to 1645 cm^{-1} is observed at higher temperature the intensity of the peak decreases. The observed change can be attributed to a transition from an ordered structure to a disordered structure and the decrease at 1645 cm^{-1} to an increased formation of free urea units. In the case of the N-H vibration, a decrease of the intensity and a broadening of the peak to higher wavenumbers were observed with increasing temperature.

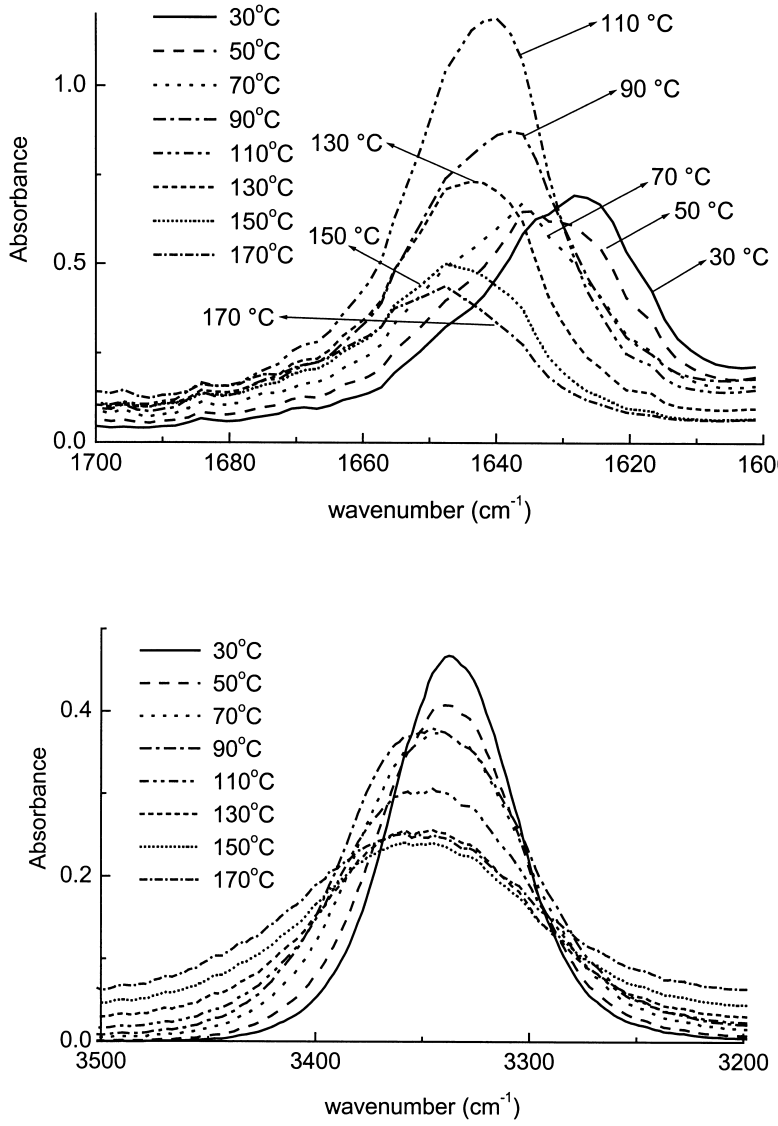


Figure 2. Temperature dependent infrared spectra of polymer A2 recorded at different temperatures around 1650 cm^{-1} (carbonylvibration) and 3350 cm^{-1} (region of N-H vibration) (see text).

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

diamino siloxane 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.

Thermoreversible silicone gels are of principal interest for several applications in cosmetics. [9,10] Therefore, polymers were tested with respect to the potential to gel silicone fluids such as cyclosilicones for example DOW 245 which is used as ingredient in cosmetic formulations. This fluid consists of tetra-, penta- and hexacylcodimethylsiloxane derivatives. As a general procedure for the preparation of the gels the polymer is heated in the silicone solvent until the polymer is completely 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.[11-14] In our study we used a visible observation. During the gelation the temperature was measured within the gel.

Table 2 summarizes the gelation behavior of the different polymers at a concentration of 20 wt% in DOW 245. If the siloxane segment is too short as it is in A 1 the polymer is not soluble in DOW 245 even at elevated temperatures. The polymers with longer siloxane units are soluble and the gelation temperature decreases with an increase of the length of the siloxane segments. However, if the longest siloxane unit was used the polymer does not form a gel.

Table 2. Gel properties of the polymers A1-A4 in cyclodimethylsiloxane (DOW 245) at a concentration of 20 wt%.

Number	Gel point (°C)	Gel properties
A1	-	polymer not soluble
A2	85	clear gel
A3	48	clear gel
A4	-	viscous turbid liquid

The influence of the polymer content on the gelation temperature was studied. Here the results for polymer A2 are reported. Figure 3 shows the dependence the polymer concentration of A2 on the gel point.

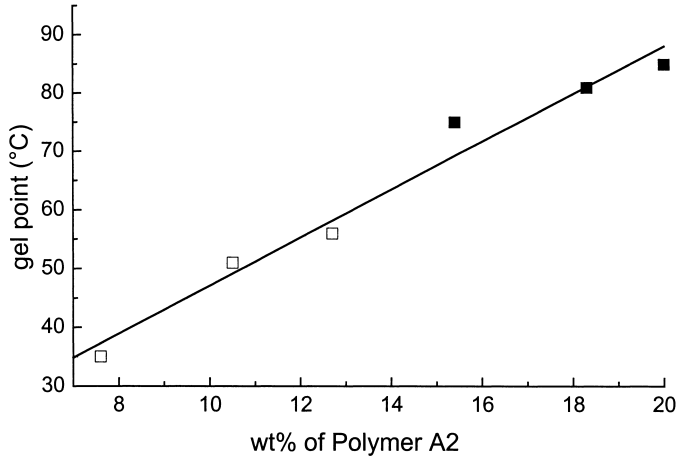


Figure 3. Dependence of the gel point of polymer A2 on the concentration in cyclodimethylsiloxane (DOW 245) (open symbols: turbid gels, closed symbols: clear gels).

It can be observed that the gel point increase as expected with increasing polymer content. Another interesting observation is that the gel is turbid if the concentration of polymer is below 15 wt% of the polymer A2 in DOW 245. The polymer does not forming 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.

In addition to binary mixtures also ternary mixtures containing two ureasiloxane polymers were investigated. The results on mixtures of A2 with a siloxane segment molecular weight of 2600 g/mol and A3 with a siloxane segment molecular weight of 5200 g/mol were used in a ratio of 2:1, 1:1 and 1:2. Polymer A2 has a higher gelpoint but is less soluble than polymer A3. Table 3 summarizes the results.

Table 3. Gel properties of ternary mixtures of the polymer A2 and A3 in the cyclosiloxane fluid DOW 245 at a concentration of 10 and 20 wt%.

Number	20 wt% of polymer		10 wt% of polymer	
	gel point (°C)	gel properties	gel point (°C)	gel properties
A2	85	clear gel	51	turbid gel
A2/A3 (2:1)	76	clear gel	66	turbid gel
A2/A3 (1:1)	74	clear gel	56	slightly turbid gel
A2/A3 (1:2)	70	clear gel	54	clear gel
A3	48	clear gel	-	viscous and clear liquid

All mixtures with 20 wt% of the polymer resulted in clear gels. The gel point decreases with lowering the concentration of the polymer A2. Remarkably the mixtures with only 10 wt% of the polymers are turbid at a higher content of A2. If the concentration of A3 is higher the gels becomes clear. Polymer A3 alone is not able to form a gel in DOW 245. Figure 4 illustrates the dependence of the gelation point. The clear gels are shown as closed symbols.

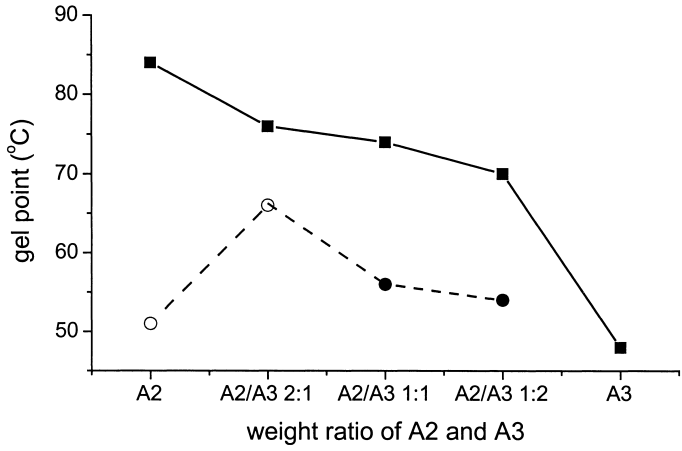


Figure 4. Dependence of the gel point on the ratio of the polymers A2 and A3 in the silicone fluid DOW 245 (open symbols: turbid gels, closed symbols: clear gels; circle: 10 wt% of polymer, square: 20 wt% of polymer).

Synthesis and properties of polymers with different structure of the urea segment

In order to investigate the influence of the hard segment on the properties another series of polymers polyureas siloxanes with different hard segments were synthesized. The synthesis of the urea-siloxane polymers B1-B5 is outlined in the following reaction scheme. In all cases commercially available diisocyanates were used. The used telechelic amino terminated siloxane had a molecular weight (M_n) of 2600 g/mol.

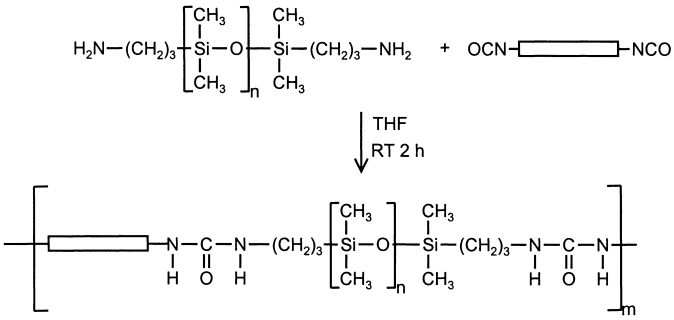


Table 4 summarizes the molecular weight (M_n) of synthesized urea-siloxane polymers and their properties in the silicone fluid at a concentration of 20 wt%. All polymers except B5 are clear and colorless highly elastic solids. B5 is of slightly yellow color.

Table 4. Molecular weight and gelation properties of main-chain urea-siloxane polymers with different diisocyanates.

Number	Diisocyanate OCN-R-NCO	Molecular weight (M_n) (g/mol)	Gel properties 20 wt% of polymer
B1	R = hexamethylene	78 400[a]	clear gel, gel point: 85 °C
B2	R = dodecamethylene	36870[a]	clear gel, gel point: 60 °C
B3	R = 2,2,4- and 2,4,4-trimethyl hexamethylene[b]	75300[a]	clear highly viscous solution
B4	R = isophorone	107600[a]	clear gel, gel point: 92 °C
B5	R = 2,4-toluene	19550[a]	clear yellow gel, gel point: 73 °C

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

The Table 4 demonstrates the influence of the hard segment on the gel points. A comparison of B1 and B2 shows that a longer alkyl chain leads to a lower gel point. Consequently the preparation temperature for the gel is also lower. B1 must be heated to 160 °C until the polymer is completely dissolved in DOW 245 whereas B2 only to 130 °C. B1 and B2 form clear gels. The system with B3 does not form a gel. This can be explained by a disorder of the structure of the hard segment as a result of the methyl groups in the side chain and the mixture of the isomers. An aliphatic ring in the polymer (B4) raises the gel point to 93 °C and whereas an aromatic ring (B5) lowered the gel point to 73 °C. In both cases clear gels were obtained.

Conclusion

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 soft segment is important for the dissolution of the polymer in the silicone solvent. If the length is too short (1000 g/mol) the polymer is not soluble. If the siloxane unit is too long, the concentration of the hard urea segment is too low and the polymer cannot gel the silicone solvent. Based on the experimental observations best length of the soft segment is a molecular weight of 2500-5000 g/mol. The hydrogen bonds of the hard segment are responsible for the physical crosslinking. If the hydrogen bonds of the urea unit are too disordered the gel point decreases and no gel is formed. The strength of the bonds between of the hard segment should not be too high, in view of the insolubility in the solvent.

Acknowledgments

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