

Segmented organosiloxane copolymers.

1. Synthesis of siloxane–urea copolymers

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Siloxane–urea linked segmented copolymers were synthesized from α,ω -bis(aminopropyl)polydimethylsiloxane oligomers and various aromatic and cycloaliphatic diisocyanates such as MDI, TDI and H-MDI. Molecular weights of the siloxane oligomers were varied in the range of 1000–4000 g mole⁻¹ and high molecular weight linear copolymers were obtained by employing homogeneous solution polymerization techniques. The solvent used during the reactions has a very critical role on the average molecular weight of the final product. Bis(2-ethoxyethyl) ether (EEE) and THF were most useful. Chain extenders such as aliphatic or cycloaliphatic diamines were also used in some reactions and in this case polar cosolvents such as NMP were also required. The yields were usually very high and the amorphous products obtained from the simple stoichiometric linking reaction were soluble in various common organic solvents. Formation of urea linkages during the polymerization were followed by FTi.r. spectroscopy. The copolymers were characterized by g.p.c. and intrinsic viscosity measurements, FTi.r., n.m.r. and thermal analysis. All these results together with mechanical characterization described in the accompanying second paper of this series indicate the formation of novel, segmented elastomeric siloxane–urea copolymers.

(Keywords: siloxane; segmented; copolymers; polyurea; elastomer; diisocyanate)

INTRODUCTION

The unique properties of siloxane polymers have led to their widespread application in many diversified fields. These properties of polysiloxanes arise mainly from the nature, physical and chemical characteristics of the siloxane (Si–O) bond which is well documented in the literature^{1–5}. The outstanding properties of polydimethylsiloxane (PDMS) polymers include their extremely low glass transition temperatures (–123°C), high thermal and oxidative stability, u.v. resistance, low surface energy and hydrophobicity, good electrical properties and high permeability to many gases. Moreover, their physical properties show only a very small variation over a wide temperature range. Finally, and perhaps most importantly, they have very good biocompatibility and are of great interest for biomaterials that will be utilized in the presence of blood.

Polydimethylsiloxane (PDMS) rubbers require extremely high weight average molecular weights to develop useful properties. Although it is an apparent solid at a molecular weight of about 500 000 it still exhibits cold flow and is well known to be very weak mechanically at room temperature. PDMS must generally be chemically crosslinked in order to be used as an elastomer. However, unfilled polydimethylsiloxane vulcanizates have very low tensile strengths (2–5 kg/cm²) and in most commercial applications they are usually filled (up to 40–50 per cent

by weight) with finely divided high surface area silica.

A very important way to improve the mechanical strength while still retaining the desired properties of siloxanes is via the controlled synthesis of AB, ABA or (AB)_n block or segmented copolymer architecture, where the soft component is polydimethylsiloxane. This approach has been used extensively by many workers and various segmented or block siloxane copolymers have been synthesized and characterized^{4,5}. In such systems the hard segments consist of either crystalline structures with high melting points or amorphous structures with high glass transition temperatures and include polystyrene^{6,7}, poly(methylmethacrylate)^{6,8}, poly(α -methylstyrene)⁹, polydiphenylsiloxane^{10,11}, polyamide¹², polycarbonate¹³, polysulphone¹⁴, polyurethane^{15,16}, etc.... These copolymers behave as thermoplastic elastomers and their ultimate properties depend on the type and nature of the hard segments, relative molecular weights, composition and/or ratio of the hard and soft segments⁴.

In our laboratories we have been working on the synthesis and characterization of various siloxane containing segmented and block copolymers for several years^{17–19}. Recently, we were able to synthesize well defined siloxane copolymers with urea, amide and imide hard segments. Some of our preliminary results on these novel systems have already been published^{20–23}. In this paper we will discuss the detailed synthetic procedures for preparation of segmented siloxane–urea copolymers based on aromatic MDI, TDI and cycloaliphatic H-MDI. The effect of solvent and chain extenders on the reaction systems will also be discussed. Structural and physical characterization of the products will also be given. The accompanying paper will discuss the mechanical and morphological characterization of these novel systems.

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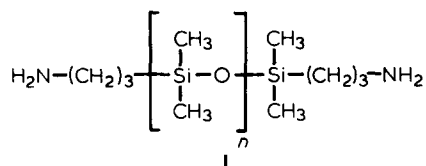
EXPERIMENTAL

Materials

All diisocyanates discussed in this paper were generously supplied by Mobay Chemical Co.

MDI was refluxed with toluene to azeotrope the moisture and then was distilled under vacuum (purity 99.8%). TDI was distilled under vacuum (purity 99.9%). H-MDI was used as received, since it was possible to show that the purity was better than 99.7% (by butylamine titration).

α,ω -Bis(aminopropyl)polydimethylsiloxane oligomers, **1**, were synthesized in our laboratories²⁴. For this purpose



cyclic octamethyltetrasiloxane (D4) was equilibrated with 1,3-bis(γ -aminopropyl)tetramethyldisiloxane in bulk using tetramethyl ammonium hydroxide, potassium hydroxide or the corresponding silanolate initiators. The reactions were performed at 80–100°C for at least 24 h which was sufficient time for equilibration reactions. After deactivating the catalyst, the samples were stripped under high vacuum in order to remove low molecular weight cyclic side products which are typically present at a level of 12–15% by weight in such equilibration reactions²⁵. A list of the oligomers synthesized and used throughout this work is provided in Table 1. FTi.r. and ¹H-n.m.r. spectra of the oligomer with $\bar{M}_n=1140$ are reproduced in Figures 1 and 2 respectively. These spectra were obtained

Table 1 Characteristics of α,ω -bis(aminopropyl)polydimethylsiloxane oligomers used in polymerization reactions

No.	\bar{M}_n (Titration)	No. [Si(CH ₃) ₂ O] Repeat Units	T_g (°C)
1	1140	13	-118
2	1770	22	-121
3	2760	35	-123
4	2780	35	-123
5	3580	46	-123
6	3660	47	-123
7	3740	48	-123

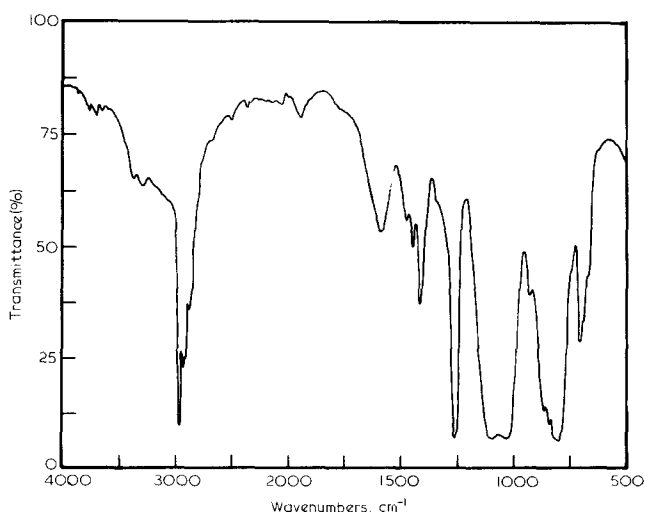


Figure 1 FTi.r. spectrum of α,ω -bis(aminopropyl)polydimethylsiloxane oligomer, $\bar{M}_n=1140$ g mole⁻¹ [Neat on KBr disc]

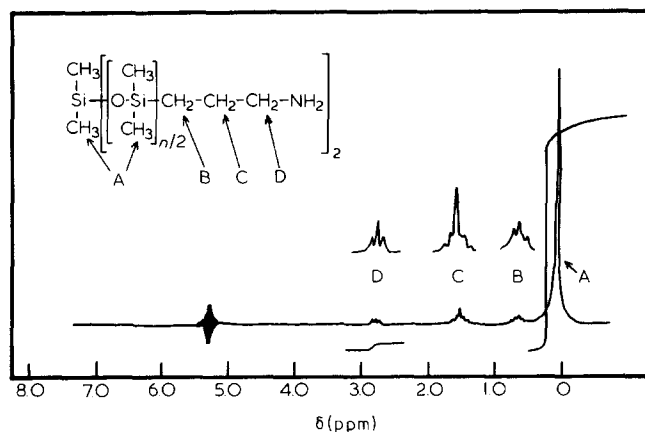


Figure 2 ¹H-n.m.r. spectrum of α,ω -bis(aminopropyl)polydimethylsiloxane oligomer, $\bar{M}_n=1140$ g mole⁻¹. [CDCl₃ solution]

with a Nicolet MX-1 FTi.r. and Varian EM-390 NMR at room temperature. The FTi.r. spectrum shows two peaks which are assigned to the H-bonded N–H stretching at 3365 (Assym) and 3290 cm⁻¹ (Sym), respectively. There is also a broad band around 1620 cm⁻¹ due to N–H bending which is characteristic of primary aliphatic amines. The broad band between 600 and 900 cm⁻¹ is due most probably to N–H wagging which is overlapped with CH₃ rocking absorptions (810 and 860 cm⁻¹). Strong Si–O–Si stretching absorptions at 1020 and 1090 cm⁻¹ are representative of the siloxane backbone. In addition, the ¹H-n.m.r. spectrum also confirmed the structure **1** (Figure 2).

p-Aminocyclohexylmethane (PACM-20) was generously provided by DuPont and was used as the chain extender in some reactions. It was purified by fractional distillation under vacuum before use. The diamine 1,6-Diaminohexane (HMDA) was also used as a chain extender in some cases.

The reaction solvents utilized were tetrahydrofuran (THF), bis(2-ethoxyethyl)ether (EEE) and *N*-methylpyrrolidone (NMP) (Aldrich). They were dried over CaH₂ or metallic sodium by refluxing and then were fractionally distilled under atmospheric pressure (THF, only) or vacuum.

Reaction procedure

All reactions were carried out in 4 necked round bottom reaction flasks fitted with dropping funnel, condenser, gas inlet and thermometer. Stirring was provided via a magnetic stirrer.

Calculated amounts of diisocyanate and low molecular weight polydimethylsiloxane oligomer (PSX) were separately weighed into glass stoppered Erlenmeyer flasks. They were added into the reaction flask under argon via a dropping funnel. The concentrations of the reactants and solvent could be varied, but typically the diisocyanate was about 0.10–0.15 molar and the total weight of derived segmented copolymer was 10–15 g/100 ml. The reaction was started by the dropwise addition of the PSX solution at room temperature to the liquid isocyanate solution in the reaction flask. The reactions were all relatively rapid, as expected. An increase in the viscosity of the system was easily noticeable towards the end of the PSX addition. There was also a slight increase (2–4°C) in the temperature of the system as expected. However, after the addition was completed it was necessary to heat the solution to 50–

60°C for several hours (depending on the reaction system) to ensure very high extents of reaction and hence high molecular weight. In some cases, when the increase in viscosity was too high, a small amount of NMP was added in order to reduce the solution viscosity such that effective stirring could be maintained. When chain extenders were used, they were generally weighed together with PSX into the same flask and the same reaction procedure was followed.

The products obtained were isolated by coagulation in isopropanol or isopropanol/water (90/10) mixture, washed several times with the alcohol, filtered and dried in a vacuum oven at 50°C until constant weights were reached. Isopropanol was utilized since it is a solvent for any unreacted oligomer or cyclic by-products.

Characterization of products

Spectroscopic characterization of the starting materials and the copolymers produced were obtained by a Nicolet MX-1 FTi.r. spectrometer using solution cast films on KBr discs. A typical FTi.r. spectrum of a siloxane-urea copolymer based on PSX-1140 and MDI is given in Figure 3. The strong absorption bands around 3300 cm^{-1} (N-H stretch) and 1700 cm^{-1} (C=O stretch) confirm the formation of urea linkages. The absence of a strong absorption around 2250 cm^{-1} (N=C=O stretch) shows that the reaction is, for all practical purposes, completed. The peaks at 1260 cm^{-1} (Sym. CH_3 bending), 1020 and 1100 cm^{-1} (Si-O-Si stretching), 860 and 810 cm^{-1} (CH_3 rocking) show the incorporation of siloxane into the copolymer.

High resolution ^1H -n.m.r. spectra were recorded on a Varian EM-390 spectrometer at room temperature using CDCl_3 as the solvent. Figure 4 gives the proton n.m.r. spectrum of a siloxane-urea copolymer synthesized from PSX-1140 and MDI. The chemical shift at 0.16 ppm is due to methyl protons bonded to silicon. Very weak peaks at 1.0–2.0 ppm are due to the three methylene or propyl groups. Those at 6.6–7.2 ppm are due to aromatic protons. Urea protons probably resonate around 8.0 ppm and show only a very weak, broad band.

Intrinsic viscosities were determined in THF at 25°C using Ubbelohde viscometers. G.p.c. chromatograms were obtained by a Waters h.p.l.c., at 22°C using THF as

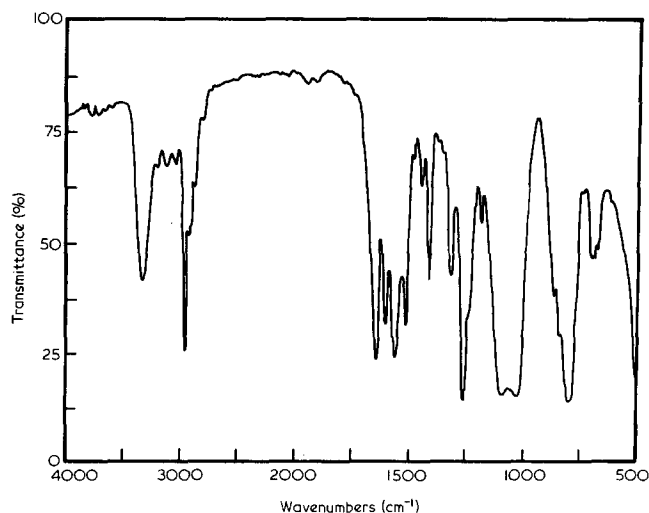


Figure 3 FTi.r. spectrum of siloxane-urea copolymer synthesized from PSX-1140 and H-MDI. [Solvent cast film on KBr disc]

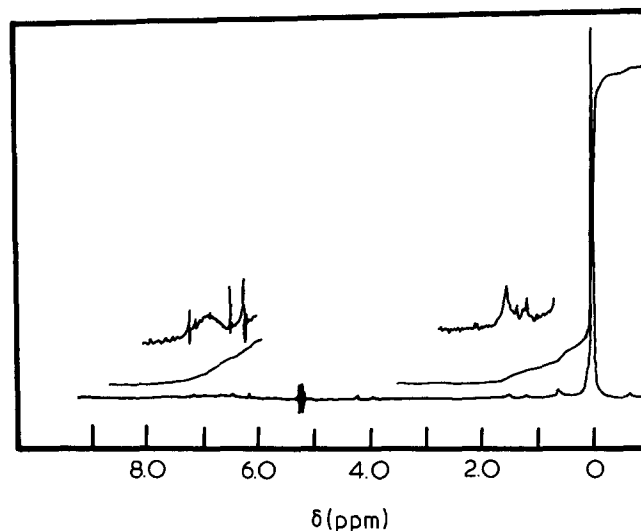


Figure 4 ^1H -n.m.r. spectrum of siloxane-urea copolymer synthesized from PSX-1140 and MDI. [CDCl_3 solution]

the solvent and styrogel columns of 10^5 , 10^4 , 10^3 and 500 Å. The flow rate was 1.0 ml min^{-1} and the polymer concentration was 0.25 g dl^{-1} .

Thermal characterization (d.s.c., t.g.a., t.m.a.) were performed on a Perkin-Elmer System 2. The thermograms were recorded under either a helium or nitrogen atmosphere, using a heating rate of 10°C/min . At least two scans were run for each sample and after each scan the samples were quenched with a cooling rate of 160°C/min .

RESULTS AND DISCUSSION

In the open literature one finds little or no detailed publications on the controlled synthesis of siloxane-urea copolymers. One patent²⁶ describes the synthesis of elastomeric threads, where siloxanes were reacted with aromatic compounds and siloxane-urea type materials were obtained. The products displayed some interesting properties such as high strength and elongation at break, and good recovery after extension. Although there is an apparent lack of research on siloxane-urea systems, there are several references to the synthesis and characterization of siloxane-urethane copolymers. The interest in these type of materials has been mainly due to their excellent blood compatibility^{27–29}. Most of the work in this field utilized the well known procedures used for polyurethane synthesis. The only difference during the reactions was the partial replacement of polyols by functional polydimethylsiloxane oligomers at various levels^{15,30,31}. However, the definition of structure and proper characterizations of the PSX 'polyol' are often insufficient.

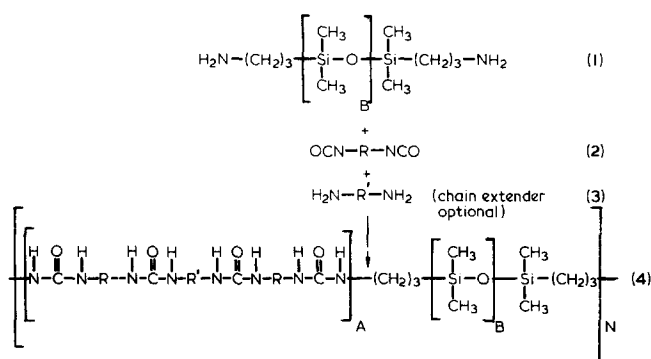
Besides these mixed polyether-polyester-polysiloxane urethanes, several other workers attempted to synthesize poly(siloxaneurethanes) utilizing various functionally terminated dimethylsiloxane oligomers. The functional groups included silanols^{32,33}, hydroxybutyl^{16,34} or hydroxypropyl³⁵ groups or others^{36,39}. The reactions were generally carried out in bulk and the products obtained were thought to be linear, but were mostly of low molecular weight. The silanol based systems were easily hydrolyzable in aqueous or alcoholic solutions¹ as one might expect, and thus would have very limited use.

In our laboratories we also investigated the kinetics of

model siloxane-urethane formation reactions³⁷. The results have shown that although these reactions were second-order up to 90–95 per cent conversions, the reaction rate was extremely slow when compared with conventional polyurethane reactions. However, we were able to synthesize linear, high molecular weight materials with good tensile strength.

After the preliminary investigation described above, we decided to use aminopropyl functional siloxane oligomers and synthesize siloxane-urea type copolymers. Interestingly, the aminopropyl functionality on the siloxane oligomer also reacts significantly slower with isocyanates than an analogous hydrocarbon amine. As one may note from the Experimental section, it was necessary to increase the reaction temperature to 50°C or higher, in order to reach very high extents of reaction. Further kinetic studies are planned to elucidate this different behaviour. Nevertheless, the advantages of such a system over siloxane-urethanes would include much faster reaction rates even at ambient temperatures, good stoichiometric control due to the directly titratable ($-\text{NH}_2$) end groups, stronger hydrogen bonding in the resultant system due to higher cohesion energy of urea groups compared to urethanes³⁸ and enhanced thermal stability of the final products. Preliminary communications of our early results on the synthesis and characterization of these novel, linear, high molecular weight, elastomeric siloxane-urea copolymers have already been published^{20,21}. In this paper we will expand our discussion and also report some of our results on the effect of diisocyanate type, solvent, temperature, catalyst and chain extenders on the reaction systems and on the properties of the final products.

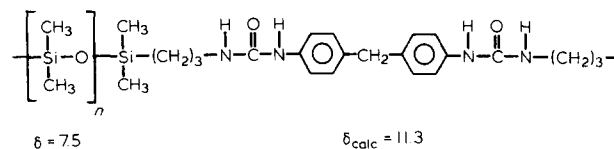
The reaction scheme for the synthesis of randomly coupled (AB)_n type segmented poly(siloxane-urea) copolymers can be written as follows:



where R and R' represent the organic backbone of the diisocyanate and the chain extender, respectively.

Effect of solvent on the reaction of polysiloxane with MDI

As we have mentioned briefly before²⁰, the choice of reaction solvent is very important in order to obtain high molecular weight, linear segmented siloxane-urea copolymers. This arises mainly due to the great difference between the solubility parameters of highly nonpolar polydimethylsiloxanes [$\delta \sim 7.5 (\text{cal}/\text{cm}^3)^{1/2}$]⁴⁰ and the highly polar urea hard segments. The solubility parameter of the hard segment based on MDI, as shown below, 5, is



calculated to be $11.3 (\text{cal}/\text{cm}^3)^{1/2}$ by using group contribution calculations⁴¹. After the preliminary studies with solvents used conventionally in the synthesis of urea or urethane type of polymers (e.g. DMAC, DMF, NMP, γ -butyrolactone) we obtained the best results with bis(2-ethoxyethyl)ether (EEE) and tetrahydrofuran (THF). They both resulted in homogeneous, clear solutions throughout the reactions whereas in others coagulation was observed in very early stages of the process. Both EEE and THF provided high polymer yields but the molecular weights of the copolymers synthesized in former (judging from intrinsic viscosities and g.p.c.) and were higher than those synthesized in the latter. Representative results are given in Table 2.

One approach to possibly explain this phenomenon is through the concept of solubility parameters. In a good solvent, which we may define as one which is highly compatible with the polymer, the liquid-polymer interactions expand the polymer coil from its unperturbed dimension, thereby increasing its end-to-end distance. This increase in the end-to-end distance should enhance the probability of collisions between the reactive ends of the growing polymer chains, thus, resulting in high molecular weights. In order for this assumption to be valid for our system, the solubility parameter value of EEE should be closer to some average value of that of siloxane-urea copolymer than the value of THF. Since the solubility parameters of EEE and siloxane-urea copolymers are not available in the literature, their values were estimated from group contribution calculations⁴¹. This calculation produced values of 8.9 and 9.6 (cal cm^{-3})^{1/2} respectively. Solubility parameter of THF is 9.1 (cal cm^{-3})^{1/2}. Since EEE and THF have almost similar δ values, it is clear that for our system, the effect of solvent

Table 2 Effect of solvent on the synthesis of siloxane-urea copolymers based on MDI

No.	Solvent	PSX		MDI (g)	Recovered yield (wt %)	$[\eta]_{\text{THF}}^{25^\circ\text{C}}$ (dl. g ⁻¹)	Reaction time (h.)	Reaction temp (°C)
		(\overline{M}_n)	(g)					
1	EEE	1140	23.02	5.03	80	0.24	2	50
2	EEE	1770	25.96	3.79	86	0.57	2	50
3	EEE	3660	25.06	1.72	96	0.63	2	50
4	EEE	3660	10.23	0.70	97	0.70	2	50
5	THF	1140	7.15	1.58	86	0.13	2	50
6	THF	1770	8.85	1.26	83	0.14	2	50
7	THF	3660	10.43	0.72	94	0.40	2	50
8	THF	3580	9.57	0.67	91	0.48	20	35

on the molecular weight of the final product cannot be explained simply by the concept of solubility parameters.

We extended the reaction times in THF up to 9 h at 50°C in order to determine whether there were any kinetic effects or possible side reactions. In the case where EEE was the solvent we were able to obtain relatively high intrinsic viscosities (>0.50 dl/g) in 2 h of reaction at 50°C, Table 2. We withdrew samples at certain time intervals during the reaction in THF. They were then coagulated in isopropanol, filtered and dried to constant weight. A plot of intrinsic viscosities of these samples (25°C in THF) versus time for the reaction between MDI and PSX ($\bar{M}_n = 3660$) at 50°C is provided in Figure 5. It appears that the reaction proceeds rapidly in early stages, resulting in a corresponding build up of molecular weight. However, the increase seems to level off after about two hours. The intrinsic viscosity value of the plateau is about 0.45 dl/g, which is considerably lower than for those polymers synthesized in EEE, at 50°C in 2 h (e.g. $[\eta] = 0.63$ and 0.70 dl g⁻¹ as given in Table 2). Although the reasons behind this are not yet well understood, one may speculate about the relative basicities of THF and EEE and thus their ability to generate complex formation with the isocyanate groups on MDI⁴². The cyclic ethers are considered to be more basic compared to their linear analogs⁴³ possibly due to the enhanced availability of the electron pairs on the oxygen, in the case of ring compound. Hence, one would expect THF to form stronger complexes with isocyanate groups on MDI, thus retarding further reaction, especially at the final stages of the process, where the increase in the molecular weight of the product is expected in such step-growth or condensation polymerizations⁴⁶.

Copolymerization studies with TDI

After the interesting results obtained with MDI, as a natural extension we tried to utilize TDI and repeat a similar series of synthesis experiments on such siloxane-urea copolymers. We utilized both EEE and THF as the reaction solvent and they gave very similar results. Table 3 provides the results obtained by using EEE as the reaction solvent. As can be seen from the Table, intrinsic viscosities of the copolymers based on TDI are much lower than that of MDI. In the literature it is well documented that for aromatic diisocyanates, when one group is reacted, the

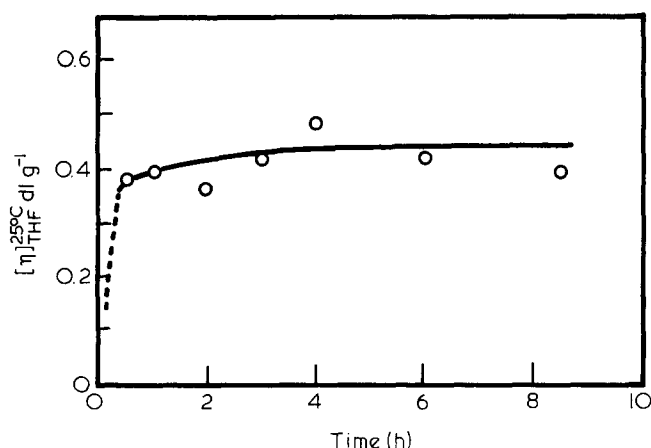


Figure 5 Intrinsic viscosity of copolymers produced as a function of time for the polymerization reaction between MDI and PSX-3580 in THF at 50°C

Table 3 Synthesis of siloxane-urea copolymers from TDI. Effect of tin octoate catalyst on reaction system

No.	PSX		TDI (g)	Cat. (wt %)	Yield (wt %)	$[\eta]_{THF}^{25^\circ C}$ (dl g ⁻¹)
	\bar{M}_n	(g)				
1	1140	14.00	2.13	—	89	0.18
2	1770	17.00	1.68	—	78	0.19
3	1140	12.20	1.85	0.01	90	0.33
4	1770	17.00	1.68	0.01	96	0.23

reactivity of the second group may be dramatically reduced due to resonance effects⁴⁴. In TDI this is more pronounced than MDI possibly also due to steric reasons. We also know that siloxanes have lower reactivities than conventional hydrocarbon systems under similar reaction conditions³⁵ as we discussed earlier. Therefore, in order to increase the rate, conversion and consequently the molecular weight of the products, we employed 0.01 per cent of tin octoate as catalyst and increased the reaction times up to 48 h. In this way, we were able to obtain slightly higher intrinsic viscosity values, which led to a significant improvement in the stress-strain behaviour of these products. Our studies on the copolymerization reactions are continuing.

Siloxane-urea copolymers based on H-MDI

As it is well known, one disadvantage of the aromatic diisocyanate based polyurethane or polyureas is their poor weatherability and sensitivity to u.v. radiation. On the other hand siloxane based copolymers exhibit some desirable properties for outdoor applications as coating materials, which include hydrophobicity, good weatherability and low friction. In order to improve u.v. stability of the siloxane-urea copolymers we have also investigated the use of a cycloaliphatic diisocyanate, bis(*p*-isocyanatocyclohexyl)methane, H-MDI, during the synthesis reactions. We also utilized hexamethylenediamine, HMDA, and bis(*p*-aminocyclohexyl)methane, PACM-20, as chain extenders.

Following up our earlier results with MDI and TDI, we chose EEE as the reaction solvent in these reactions. The results of these polymerizations are provided in Table 4.

During the reactions with H-MDI, we observed a slight coagulation of the copolymer as high conversions were reached. In fact, from Table 4 it is obvious that we did not obtain high conversions and consequently high molecular weights (referring to intrinsic viscosities) during these initial reactions, especially when compared to the similar series with MDI²⁰. When small amounts of NMP (~5–10% by volume) were added into the reaction system it was possible to obtain homogeneous and clear solutions. However, the yield or the intrinsic viscosity values of the products did not improve significantly.

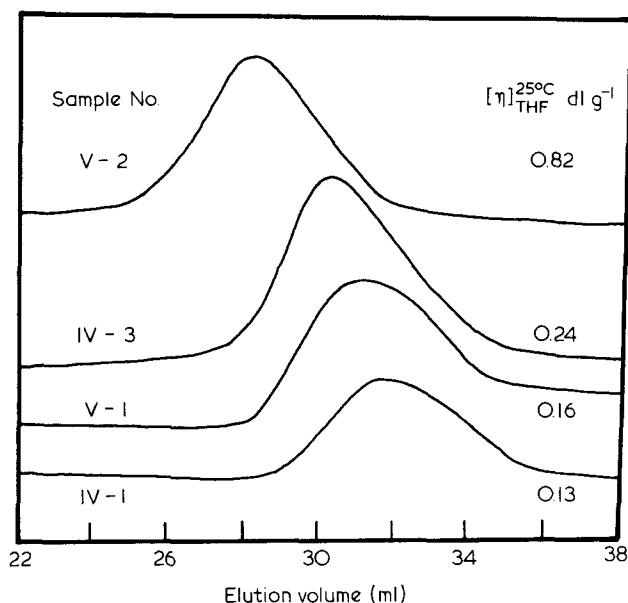
After these results with EEE, we investigated THF as the reaction solvent. Interestingly, in this case the solutions were clear throughout the reactions and no coagulation was observed. Table 5 provides the data on the synthesis reactions carried out in THF. As can be seen from Table 5, the yields are extremely high (93–98%) and the intrinsic viscosity values are much higher when compared with the corresponding systems in Table 4. It is clear that for H-MDI based segmented copolymer systems THF is a far superior reaction solvent than EEE. G.p.c. chromatograms of some of the copolymers synthesized in these solvents are given in Figure 6 in order to

Table 4 Synthesis of siloxane-urea copolymers from α, ω -aminopropyl terminated polydimethylsiloxane oligomers (PSX) and H-MDI using EEE as solvent

No.	PSX		H-MDI (g)	Yield (wt %)	$[\eta]_{\text{THF}}^{25^\circ\text{C}}$ (dl g ⁻¹)
	\overline{M}_n	(g)			
1	1140	14.34	3.28	82	0.13
2	1770	17.07	2.54	56	0.21
3	2760	19.40	1.85	84	0.24
4	3580	19.00	1.40	91	0.42

Table 5 Synthesis of siloxane-urea copolymers from α, ω -Aminopropyl terminated polydimethylsiloxane oligomers (PSX) and H-MDI using THF as solvent

No.	PSX		H-MDI (g)	Ch. Ext. (wt %)	Yield (wt %)	$[\eta]_{\text{THF}}^{25^\circ\text{C}}$ (dl g ⁻¹)
	\overline{M}_n	(g)				
1	1140	11.00	2.56	—	96	0.16
2	2780	16.90	1.60	—	98	0.82
3	3740	19.32	1.36	—	97	0.62
4 ^a	3740	14.97	1.35	0.24	94	0.50
5 ^b	3740	12.01	1.10	0.11	97	0.41
6 ^a	3740	14.28	1.73	0.58	93	0.73

^aChain Extender is PACM-20^bChain Extender is HMDA**Figure 6** G.p.c. chromatograms for siloxane-urea copolymers synthesized from H-MDI and various siloxane oligomers using EEE or THF as reaction solvent

make a better relative comparison of molecular weights.

As noted in *Table 5*, we also used some chain extenders during the reactions. We were able to obtain high yields and fairly high intrinsic viscosity values which is in contrast to the efforts with MDI^{20,42}. During these reactions, however, a small amount of NMP was needed in order to reduce the viscosity of the solutions. By increasing the polarity of the reaction system the polymer solution remained clear and homogeneous throughout the entire reaction. The thermal (t.m.a.) and mechanical properties of the products also showed marked improvements for these chain extended systems compared to the

other system, as well be discussed in the accompanying paper⁴⁵.

D.s.c. scans of all H-MDI based copolymers showed a glass transition around -120°C due to the siloxane backbone. However, though difficult, it was possible to detect a high temperature T_g in either the 'stoichiometric' or 'chain extended' systems. On the other hand t.m.a. and dynamic mechanical loss curves clearly indicated the presence of hard segments⁴⁵.

CONCLUSIONS

In this paper, we have successfully demonstrated the controlled homogeneous synthesis of randomly coupled segmented siloxane-urea copolymers from α, ω -(aminopropyl)polydimethylsiloxane oligomers and diisocyanates with well defined structures. The products displayed very interesting self-reinforced elastomeric properties due to strong urea linkages.

The reaction between diisocyanates and amine terminated polydimethyl siloxane oligomers are relatively fast even at ambient temperatures. However, to achieve high molecular weight products in fairly short reaction times, it was desirable to complete the reaction at $50-60^\circ\text{C}$. The solvent used during the reactions has a very important influence on the polymerization rate and molecular weight of the final product. In the reactions described here, bis(2-ethoxyethyl)ether (EEE) and tetrahydrofuran (THF) were found to be good solvents for the aromatic and cycloaliphatic systems, respectively. Possibly chlorinated aliphatic or aromatic solvents may also be suitable for such reactions. All of the products obtained yielded transparent films and were linear as judged by the fact they were soluble in a range of common organic solvents. They were also compression mouldable at temperatures between $150-200^\circ\text{C}$, depending on their overall structure and composition. It is thus possible to obtain products with a wide range of physical and mechanical properties by properly designing and choosing the molecular weight of the siloxane oligomers used, the structure and nature of the diisocyanate and amount and type of the chain extenders incorporated into the copolymers.

ACKNOWLEDGEMENTS

We would like to thank the Army Research Office (ARO) for supporting this research under Grant DAAG-29-80-K-0093. We would also like to thank the DuPont, General Electric (Silicones Division) and Mobay Companies for generous samples of diamines, siloxane intermediates and diisocyanates, respectively.

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