

Siloxane-Urea Segmented Copolymers

1. Synthesis and Characterization of Model Polymers from MDI and α, ω -Bis(Aminopropyl)Polydimethylsiloxane

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SUMMARY

Siloxane-urea copolymers were synthesized from MDI and α, ω -bis(aminopropyl)polydimethylsiloxane of different molecular weights by solution polymerization, using 2-ethoxyethyl ether as the solvent. Chain extenders were also employed in some reactions. Formation of urea linkages were followed by FTIR spectroscopy. The products were characterized by GPC chromatography and intrinsic viscosity measurements. Thermal (DSC) and thermomechanical (TMA) characterization of the products were also carried out. The results indicate the formation of novel, strong multiphase elastomeric siloxane-urea copolymers.

INTRODUCTION

The incorporation of low molecular weight (\bar{M}_n 1,000-5,000) poly(dimethylsiloxane) segments into the structure of different polymer chains produces block copolymers and may provide several desired improvements in the bulk and surface properties of the products thus obtained (NOSHAY and MCGRATH, 1977). These generally include a broad service temperature of the copolymer due to the very low T_g of poly(dimethylsiloxane), (-123°C), good thermal and oxidative stability and increased impact strength. Also as is well known, the siloxane segments, due to their low surface energies, tend to migrate to the air-polymer interface and provide a very hydrophobic surface to the product (NOLL, 1968, DWIGHT et al., 1979, GAINES, 1981). Moreover, siloxanes are also of interest as biomaterials (BRALEY, 1970, WARD and NYILAS, 1978) and have high oxygen permeabilities (LE DUC, et al., 1980). Therefore siloxane containing copolymers have a wide range of potential applications as elastomers, coatings, biomaterials and as our preliminary studies show, they may also be very useful in polymer blends (MCGRATH, et al., 1982a).

In our laboratories we have developed methods to synthesize siloxane oligomers with a range of molecular

weights and having various well defined difunctional termination (such as $-\text{COOH}$, $-\text{OH}$, $-\text{NH}_2$, $-\text{CH}-\overset{\text{O}}{\text{C}}-\text{CH}_2$, $>\text{NH}$, etc) (MCGRATH et al., 1982b, RIFFLE et al., 1982). These oligomers can be reacted with conventional condensation monomers and/or oligomers for the synthesis of numerous siloxane containing block copolymers having very interesting properties.

In this paper we will briefly discuss our preliminary results on the synthesis and characterization of these novel, elastomeric poly(siloxane-urea) copolymers.

EXPERIMENTAL

MATERIALS

4,4'-Diphenylmethane diisocyanate, MDI, was kindly supplied by Mobay Chemical Co. It was distilled under high vacuum before use. Isocyanate analysis indicated a purity better than 99.5% of the theoretical value. 1,3-bis(γ -aminopropyl)tetramethyldisiloxane (DSX), \bar{M}_n was a product of Silar Laboratories, Inc. Amine terminated poly(dimethylsiloxane) oligomers (PSX), \bar{M}_n were synthesized by base catalyzed equilibration of cyclic octamethyltetrasiloxane (D_4) and DSX (MCGRATH, et al., 1982b and RIFFLE et al., 1982). Number average molecular weights were determined by the titration of amine end groups with standard HCl in isopropanol. Table I provides a summary of the siloxane oligomers prepared and their characteristics. 1,6-Diaminohexane (DAH) was a product of Aldrich Chemical Co., and was vacuum distilled before use. The solvents used were

TABLE I

Molecular Weights and Glass Transition Temperatures of α,ω -Bis(aminopropyl)polydimethylsiloxane Oligomers Used in Polymerization Reactions

\bar{M}_n (Titration)	No. $[-\text{Si}(\text{CH}_3)_2\text{O}-]$ Repeat Units	T_g^* ($^{\circ}\text{C}$)
1,000	11	-118
1,140	13	-118
1,770	22	-121
2,420	30	-123
3,670	47	-123

* by DSC, $10^{\circ}\text{C}/\text{min}$ heating rate.

2-ethoxyethyl ether (EEE) and dimethylacetamide (DMAC) (Aldrich Chemical Co.). They were purified by refluxing over metallic sodium and calcium hydride, respectively and then fractionally distilled under vacuum.

POLYMERIZATION PROCEDURE

Reactions were carried out in a round bottom, three-neck flask fitted with a dropping funnel, dry N₂ inlet and thermometer. During the polymerization either a one-step or two-step procedure was followed depending on the desired structure of the final product.

In the one-step procedure, equimolar amounts of MDI and PSX were weighed into separate, glass stoppered Erlenmeyer flasks and both were dissolved in EEE. Then, the MDI solution was transferred into the reactor and the PSX solution into the dropping funnel. The reaction was carried out by dropwise addition of PSX into the MDI solution at room temperature. After all the PSX has been added, the temperature of the system was increased to 50°C and maintained for 1 hour to insure that the reaction would be driven to very high conversions.

The two-step procedure involved first capping the PSX with excess MDI. In the second step, the chain extender (DSX or DAH) was dissolved in DMAC and added dropwise from the addition funnel at room temperature.

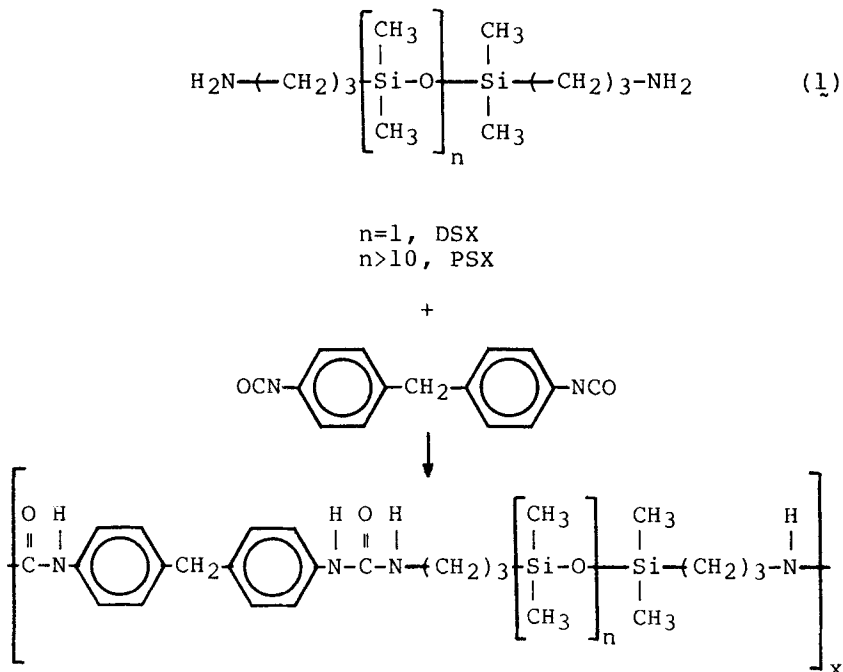
Polymers obtained were coagulated in 80/20 v/v methanol/water mixture, filtered and washed several times with methanol. They were dried in vacuum oven at 50°C overnight. Yields were determined gravimetrically. No crosslinking was observed during any of these reactions.

CHARACTERIZATION OF THE PRODUCTS

Dilute viscosity measurements were carried out in either THF or DMAC at 25°C using an Ubbelohde Viscometer. GPC chromatograms were obtained by a Waters HPLC, at 22°C using THF as the solvent and styrogel columns of 10⁵, 10⁴, 10³, and 500Å. FTIR spectra were recorded on a Nicolet MX-1 spectrometer using solution cast films on KBr discs. Thermal characterizations were performed on a Perkin Elmer System 2. DSC scans were recorded under helium atmosphere with a heating rate of 10°C/min. TMA penetration curves were obtained with a load of 10g and 10°C/min heating rate. Films used in the above tests were prepared by compression molding at 190°C, for 10 minutes.

RESULTS AND DISCUSSION

The polymerization reaction between amine terminated poly(dimethylsiloxane) oligomers and MDI, which yields a siloxane-urea copolymer can be written as follows:



It is similar to conventional amine-isocyanate systems in the sense that the reaction is very fast at ambient temperatures (YILGÖR, et al., 1982). A critical problem in this type of copolymerization reaction with a siloxane oligomer is the choice of the solvent. As is well known, siloxanes are extremely non-polar and have very low solubility parameters. On the other hand, urea linkages are hydrogen bonded and are highly polar thus conventional polyureas have much higher solubility parameters than siloxanes. Therefore, the solvent(s) used during the reaction is very critical if one wishes to prepare high molecular weight products. For this system 2-ethoxyethyl ether and dimethylacetamide (as cosolvent during chain extension) yielded very good results. The solutions appear to be homogeneous and no precipitation is observed during the reactions.

Data describing the polymerization reactions are shown in Table II.

TABLE II

Synthesis of Siloxane-Urea Segmented Polymers From α,ω -Bis(aminopropyl)polydimethylsiloxane, MDI and (Optionally) Chain Extenders

Sample No	MDI (g)	PSX		DSX (g)	DAH (g)	Yield (%)	$[\eta]_{\text{THF}}^{25^\circ\text{C}}$ (dl/g)
		M_n	(g)				
1	0.73	1,000	2.89	--	--	93.9	0.23
2	1.51	1,000	2.62	0.83	--	91.9	0.31*
3	5.08	1,140	23.02	--	--	76.5	0.24
4	1.41	1,770	9.94	--	--	93.4	0.51
5	0.50	2,420	4.82	--	--	95.9	0.83
6	0.56	2,420	4.12	0.135	--	94.1	0.42
7	0.70	3,670	10.23	--	--	97.0	0.70
8	0.45	3,670	3.83	--	0.087	93.9	--
9	2.14	--	--	2.10	--	92.0	0.59*
10	2.10	2,420	7.32	--	0.62	91.6	--

* Viscosity measured in DMAC

As can easily be seen, the yields are very high and intrinsic viscosities are in an acceptable range for such siloxane containing copolymers. When compression molded at 190°C, all samples, except numbers 4 and 8 yielded transparent films. FTIR spectrum of sample 4 is given in Figure 1. The strong

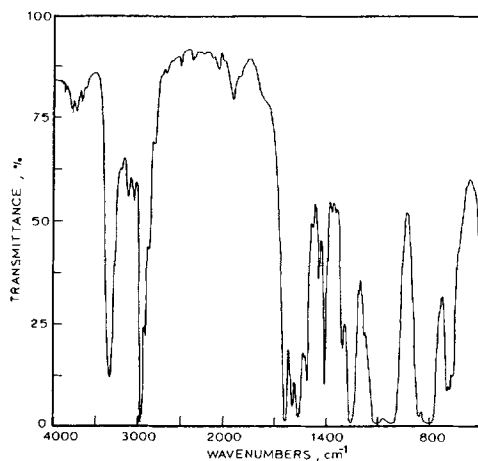


Figure 1. FTIR Spectrum of Sample 4 (Film on KBr disc)

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 band around 2250 cm^{-1} (due to NCO group) shows that the reaction is completed. The presence of the peaks at 1260 cm^{-1} (Sym. CH_3 bending), 1065 cm^{-1} (Si-O-Si stretch), 864 and 810 cm^{-1} (CH_3 rocking) show the incorporation of the siloxane into the product.

The GPC traces of THF soluble products are given in Figure 2. As can be seen, the peak maxima are in good agreement with the intrinsic viscosities.

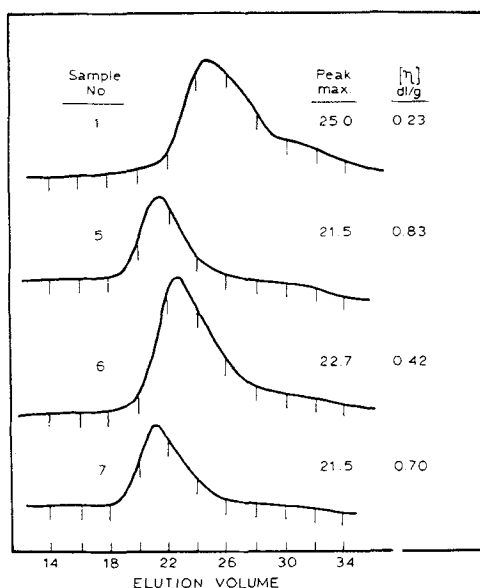


Figure 2. GPC Chromatograms of Siloxane-Urea Copolymers

Glass transition temperatures of the polymers are given in Table III. In all of the products a sharp transition for siloxane, around -120°C , was obtained. The control, Sample 9, which consists of only DSX and MDI, has no low temperature T_g as expected, but has one at $139-140^\circ\text{C}$. No crystallinity could be detected either at low (e.g. $<-50^\circ\text{C}$) or high ($<250^\circ\text{C}$) temperature. In the chain extended systems, no high temperature T_g 's were detected by DSC. This is most probably due to the very low levels of chain extenders used.

TABLE III

Glass Transition Temperatures of
Siloxane-Urea Copolymers

Sample No.	PSX		Tg (°C)
	Mn	Wt %	
1	1,000	79.8	-118
2	1,000	52.8	-118
5	2,420	90.6	-121
6	2,420	85.6	-122
7	3,670	93.6	-123
8	3,670	87.7	-123
9*	--	--	+139

* Control copolymer of DSX and MDI

In Figure 3, the TMA penetration curves for several copolymers provide a good picture of the transition behavior and the strength of the polymers obtained. Sample 9, which again is a control, shows only one penetration at temperatures above 100°C which is no doubt due to the glass transition. This is in good agreement with the DSC result. Samples 5 and 6, which were based on PSX of molecular weight 2,420 show three penetrations. One is in the very low temperature region, due to the siloxane backbone, the second is in the range of 60-80°C and the third one is above 160°C due to the flow of the polymer. The second penetration may be due to the softening of very small amount of hard

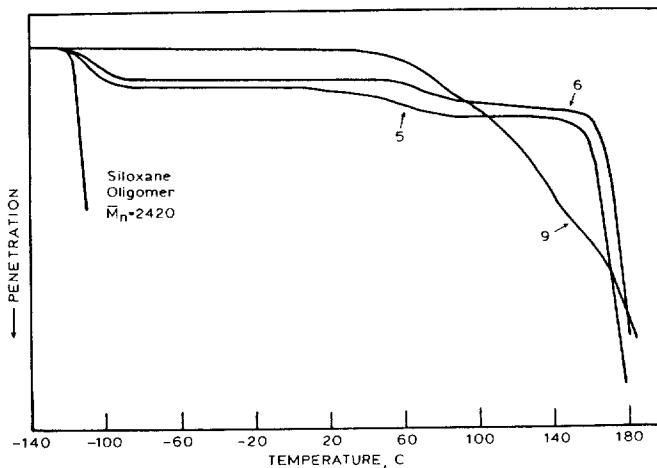


Figure 3. TMA Penetration Curves for Siloxane-Urea Copolymers

segments present in the chains. Our studies on the dynamic mechanical properties of the polymers also show a loss peak in this range. The strength and the service temperature range of these novel siloxane-urea copolymers can easily be seen by comparing the curves 5, 6 with 9 and that for siloxane oligomer of Mn 2,420, which does not have any strength above its Tg.

As a conclusion, we can say that by using amine terminated siloxane oligomers of different molecular weight and a diisocyanate, it is possible to synthesize novel, segmented elastomers in high yields, which have very interesting and useful chemical, physical and mechanical properties that may find application in various fields.

Further development of the solvent system used during the reactions is continuing. We are also investigating the effect of variations in the structures of siloxane oligomers, diisocyanates and chain extenders used on the properties of the products. Research on the detailed morphological and mechanical characterization of the polymers is also continuing and some of these results are discussed in the next paper of this issue.

REFERENCES

- BRALEY, A., *J. Macromol. Sci., Chem.*, A4(3), 529 (1970)
 DWIGHT, D. W., BECK, B. R., RIFFLE, J. S., and MCGRATH, J. E., *Polymer Preprints*, 20(1), 702 (1979)
 GAINES, G. L., *Macromolecules*, 14(1), 208 (1981)
 LE DUC, L., BLANCHARD, L. P., and MALHOTRA, S. L., *J. Macromol. Sci., Chem.*, A14(3), 389 (1980)
 MCGRATH, J. E., YILGÖR, İ, TRAN, C., and RIFFLE, J. S., Unpublished Results, 1982a
 MCGRATH, J. E., RIFFLE, J. S., YILGÖR, İ., BANTHIA, A. K., and SORMANI, P., *ACS Org. Coat. Appl. Polym. Sci., Proc.*, 46, 693 (1982b); *Ibid*, ACS Symposium Series, "Initiation of Polymerization", in press, 1982
 NOLL, W. *CHEMISTRY AND TECHNOLOGY OF SILOXANES*, Academic Press, N.Y., 1968
 NOSHAY, A., and MCGRATH, J. E. *BLOCK COPOLYMERS OVERVIEW AND CRITICAL SURVEY*, Academic Press, N Y., 1977
 RIFFLE, J. S., YILGÖR, İ, BANTHIA, A. K., WILKES, G. L., and MCGRATH, J. E., *Org. Coat. Appl. Polym. Sci., proc.*, 46, 397 (1982); *Ibid*, Epoxy Resins, R. S. Bauer, Edit., ACS Symposium Series, in press, 1982
 WARD, R. S., Jr., and NYILAS, E., *ORGANOMETALLIC POLYMERS*, Academic press, N.Y., p. 219, 1978
 YILGÖR, İ., WILKES, G. L., and MCGRATH, J. E., *Polymer Preprints*, 23(1), 286 (1982)