

D₂-*m*-Carboranesiloxanes. VIII. Preparation and Characterization of Carboranesiloxane/Polysulfone Alternating Block Copolymer

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Synopsis

A D₂-*m*-dodecacarboranesiloxane containing alternating block copolymer $\{A-B\}_n$ was prepared by the reaction of a ureidosilane-terminated polysulfone hard block with a carboranesilanol-terminated carboranesiloxane oligomer. The resulting block copolymer exhibited thermoplastic elastomeric behavior. This unique polymer had excellent thermal stability up to 400°C.

INTRODUCTION

The development of thermoplastic elastomers represents one of the most significant contributions to science and technology of materials in the last decade. An incentive exists for developing thermoplastic elastomers which incorporate the elastomeric capabilities and the outstanding thermal resistance of D₂-*m*-carboranesiloxanes. Alternative low-*T_g* polymer segments do not possess the thermooxidative capabilities of the carboranesiloxane block.

Numerous block copolymers containing poly(dimethylsiloxane) segments have been reported.¹ Their method of synthesis usually involved the reaction of chloro- or aminosilane-terminated poly(dimethylsiloxane) oligomers with a suitably substituted hard block. However, these methods were not applicable in carboranesiloxane syntheses because of the inertness of carboranesilyl chlorides toward polymerization and the deleterious side reactions from amine-containing reagents.^{2,3} Amine-containing reagents in carboranesiloxane polymerizations result in the cleavage of the carborane-silanol bond and lead to the production of low molecular weight polymers with inert endgroups.³

Therefore, a new route was developed for the synthesis of carborane-siloxane alternating block copolymers. This employed the use of bisureidosilanes, which have the high reactivity needed for reacting with carboranesilanols and the advantage of forming unreactive by-products during the condensation reactions.³⁻⁵

EXPERIMENTAL

Carboranesiloxane/polysulfone alternating block copolymer was prepared by a two-step synthetic technique. Initially a carboranesilanol-terminated carboranesiloxane oligomer was synthesized, isolated, and characterized.⁶ The carboranesiloxane oligomer was then titrated and coupled with a ureidosilane-terminated polysulfone oligomer. Experimental results are given below.

Ureidosilane-Terminated Polysulfone Oligomer

A 50-ml, one-neck flask was equipped with a septum, a nitrogen compensation needle, and a magnetic stirring bar. Methylphenyl bisureidosilane (0.44 g, 8.85×10^{-4} mole) was weighed into the 50-ml flask under nitrogen. The flask was septum sealed and 3.0 ml dried chlorobenzene was added. The flask was magnetically stirred and cooled to $-10^{\circ}\text{C} \pm 5^{\circ}\text{C}$. Azeotropically dried hydroxy-terminated polysulfone oligomer (2.66 g, 4.42×10^{-4} mole) in 14 ml chlorobenzene was titrated into the 50-ml flask over 2.5 hr using a syringe pump. After an additional cooling period of 0.5 hr at -10°C , the methylphenylureidosilane-terminated polysulfone oligomer solution was allowed to warm to ambient temperature. NMR analysis of a comparable reaction indicated nearly 100% ureidosilane termination. The ureidosilane-terminated polysulfone was not isolated but used in the following reaction.

Carboranesiloxane/Polysulfone Alternating Block Copolymer

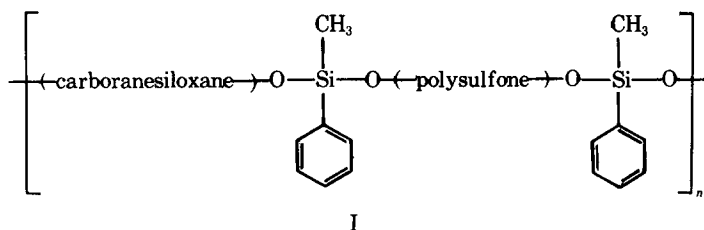
A 100-ml, one-neck flask was equipped with a septum, a magnetic stirring bar, and a nitrogen compensation needle. Carboranesilanol-terminated carboranesiloxane oligomer⁶ (2.08 g, 4.56×10^{-5} mole) was weighed into the flask. The flask was vacuum pumped at 100°C overnight to dry the oligomer sample. The flask was sealed under nitrogen, cooled, and 7-ml dried chlorobenzene was added. The flask was shaken until the oligomer was dissolved.

The oligomer solution was magnetically stirred and titrated with the previously prepared chlorobenzene solution of ureidosilane-terminated polysulfone oligomer at 25°C . The titration, using a syringe pump, was continued for 2.5 hr until the block copolymer solution became extremely viscous. Approximately 10% of the unreidosilane-terminated polysulfone solution was added. Carboranedisilanol (0.02 g, 6.8×10^{-5} mole) in 10 ml dried chlorobenzene was rapidly added to the reaction to terminate the block copolymer. The reaction was stirred overnight and then diluted with ~ 50 ml of chlorobenzene to lower the viscosity. The copolymer solution was removed from the flask and further diluted with ~ 150 ml of chlorobenzene prior to precipitation from 2 liters methanol. The isolated block copolymer was vacuum dried at 100°C . The recovered block copolymer weighed 2.21 g (94.0%), $RV = 3.65$ dl/g in CHCl_3 at 25°C .

RESULTS AND DISCUSSION

An alternating block copolymer, $\{A-B\}_n$, was synthesized by coupling a carboranesilanol-terminated carboranesiloxane oligomer with a methylphenylureidosilane-terminated polysulfone oligomer. The block copolymer I exhibited a molecular weight of about 10^6 . The molecular weight of the block copolymer was equivalent to the molecular weights previously obtained for ul-

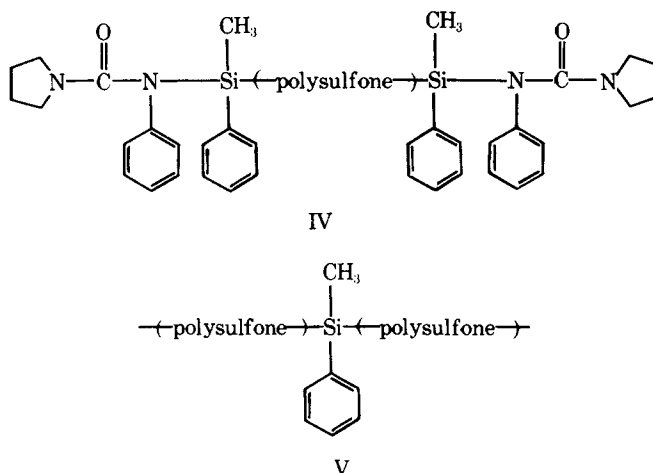
trahigh molecular weight D₂-*m*-carboranesiloxane polymers.⁶



Preparation of Block Copolymers

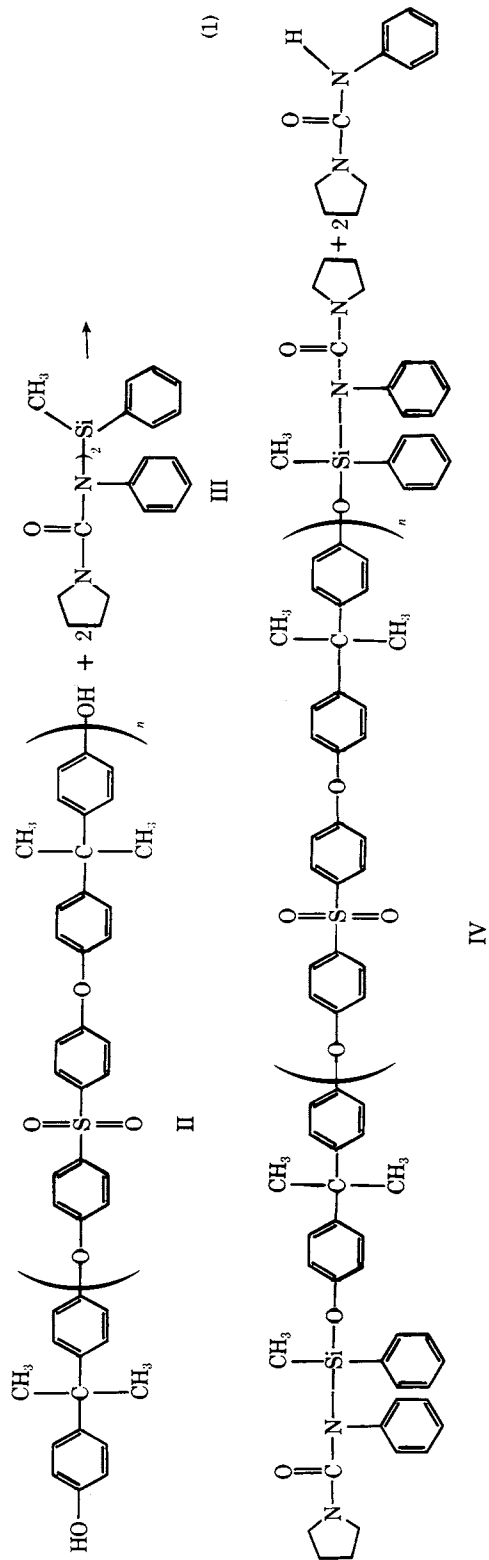
The synthesis of carboranesiloxane/polysulfone alternating block copolymers was performed in a two-step sequence. Step 1 of the reaction sequence, eq. (1), consisted of adding one molar equivalent of a hydroxy-terminated polysulfone oligomer II ($\bar{M}_n = 6020$, D.P. = 13.1) to two molar equivalents of methylphenylbisureidosilane, III, in chlorobenzene at $-10^\circ\text{C} \pm 5^\circ\text{C}$. (See Scheme I.)

A particularly useful technique was developed in which we were able to analyze the degree of termination product IV or internal (coupling) product V by using 100 MMz ¹H-NMR spectroscopy to evaluate the siliconmethyl group as shown in Figure 1. Thus, a ureidosilane-terminated polysulfone oligomer, IV, was prepared at $-10^\circ\text{C} \pm 5^\circ\text{C}$ in near 100% purity by NMR analysis. This was possible because of the higher reactivity of the bisureidosilane- than the monoureidosilane-terminated oligomer:



Step 2 of the reaction sequence, eq. (2), consisted of stoichiometrically titrating a carboranesilanol-terminated carboranesiloxane oligomer,⁶ VI ($\bar{M}_n = 45,560$, D.P. = 122), with the previously prepared ureidosilane-terminated polysulfone

Scheme I



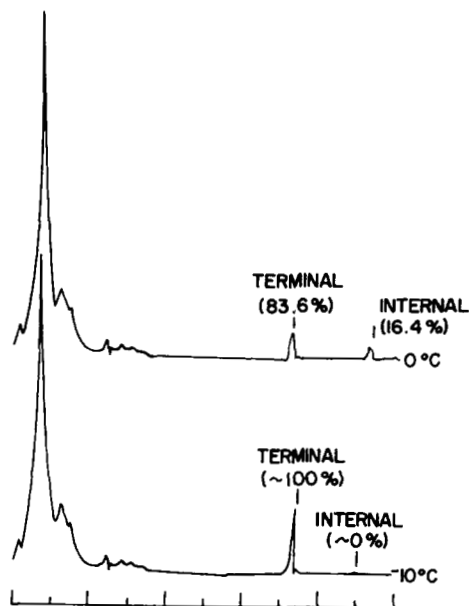
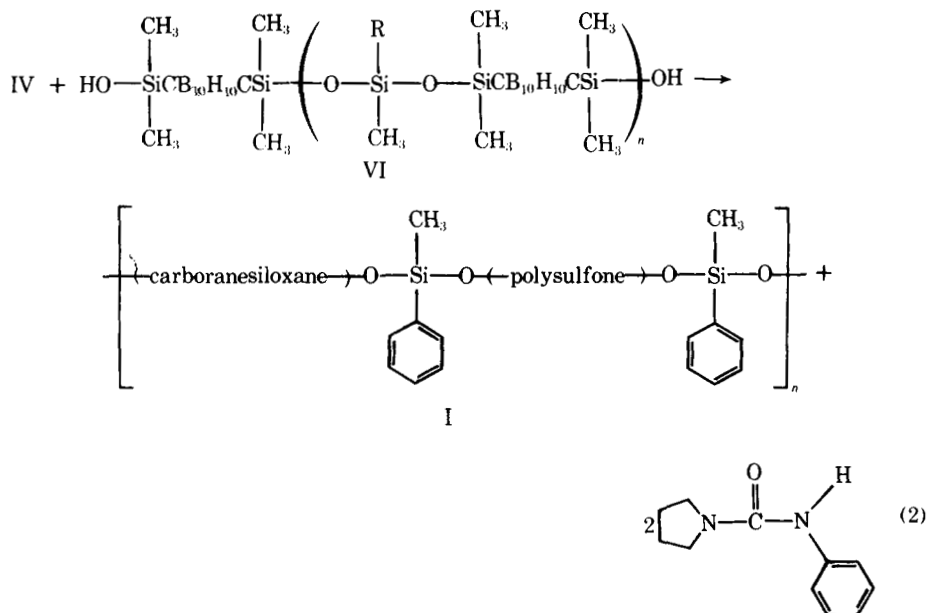


Fig. 1. NMR analysis of termination vs coupling of polysulfone oligomer.

oligomer IV to alternately couple the two oligomers. The titration to couple the two oligomers was continued until an extremely high solution viscosity was obtained. The reaction was then terminated with excess carboranedisilanol.



where R = CH₃, C₆H₅, (2:1)

Thermal Mechanical Properties

The mechanical properties of carboranesiloxane/polysulfone block copolymer containing 11.8 wt. % polysulfone hard block were determined over a temperature range of -25 to 200°C and appear in Table I. The mechanical properties in the temperature range of -25 to 25°C are indicative of properties between the glass transition temperature (-27°C) and the melting temperature ($\sim 53^{\circ}\text{C}$) of the carboranesiloxane soft block. The properties from 50 to 150°C are for a block copolymer above the melting temperature of the carboranesiloxane soft block which results in a sharp drop in the modulus. At a temperature of 200°C , the polysulfone hard block has surpassed its glass transition temperature (165°C) which causes a large drop in the elongation of the block copolymer.

The E/T curve (modulus versus temperature) shown in Figure 2 graphically illustrates the effect on the modulus of the polysulfone hard block in the alternating block copolymer. The modulus of the block copolymer is compared with D_2 -*m*-carboranesiloxane polymer of equivalent molecular weight⁶ and with commercial-grade polysulfone, P-1700. From the carboranesiloxane glass transition temperature (-27°C), the block copolymer softens until the melting temperature ($\sim 53^{\circ}\text{C}$) of the carboranesiloxane soft block is reached. From 53 to 270°C , an elastomeric plateau is maintained which has a higher modulus than melted carboranesiloxane polymer due to the influence of the polysulfone pseudocrosslinking effect. The glass transition (165°C) of the polysulfone hard block is seen in the block copolymer by the slight drop in modulus in the center of this elastomeric plateau. Above a temperature of 275°C , the block copolymer exhibits melt flow and finally melt failure at $\sim 375^{\circ}\text{C}$.

The curve in Figure 3 plots the resilience of the block copolymer as a function of temperature. The resiliency was retained between the glass transition temperature (-27°C) of the carboranesiloxane soft block and the glass transition temperature (165°C) of the polysulfone hard block. The block copolymer recovered its resilience after the glass transitions, as would be expected of a true elastomer. Beyond 275°C , the block copolymer begins to melt flow and lose its resilience until melt failure is achieved at $\sim 375^{\circ}\text{C}$.

TABLE I
Mechanical Properties of Carboranesiloxane/Polysulfone Alternating Block Copolymer^a

Test temperature, $^{\circ}\text{C}$	Young's modulus, psi	Tensile strength, psi	Elongation at break, %	Yield strength, psi	Yield elongation, %
-25	2070	662	210	111	6
0	795	247	200	30	14
25	352	137	200	35	25
50	70	167	320	none	none
100	70	137	400	—	—
150	70	24	240	—	—
200	35	12	75	none	none

^a 11.8 wt. % polysulfone block, 88.2 wt. % weight carboranesiloxane.

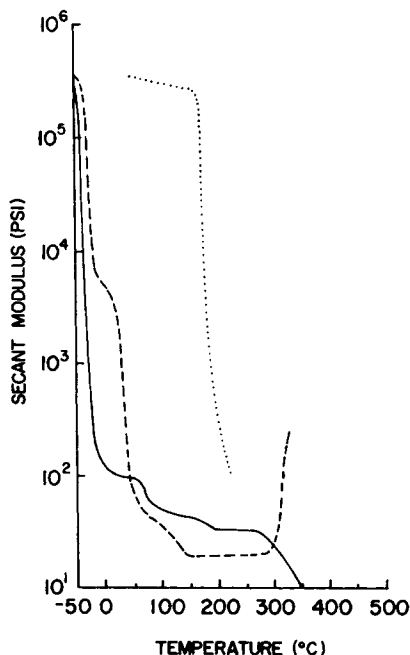


Fig. 2. Modulus vs temperature of carboranesiloxane/polysulfone block copolymer: (—) block copolymer; (---) D₂-*m*-carboranesiloxane; (···) polysulfone.

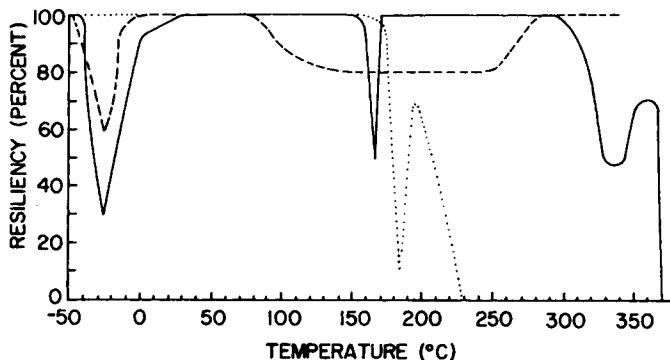


Fig. 3. Resiliency vs temperature of carboranesiloxane/polysulfone block copolymer: (—) block copolymer; (---) D₂-*m*-carboranesiloxane; (···) polysulfone.

Thermal Stability

The thermal stability of the carboranesiloxane/polysulfone alternating block copolymer was determined by thermogravimetric analysis up to 800°C. The polymer stability was determined both in air and nitrogen, by measuring the weight loss, or gain, as a function of temperature, and was compared with ultrahigh molecular weight carboranesiloxane polymer and commercial-grade polysulfone, see Figures 4 and 5. The carboranesiloxane/polysulfone block copolymer tested both in air and nitrogen had an onset of weight loss at ~400°C, which indicated good thermal stability. In air, the block copolymer had a ~12% weight loss at 500°C, which corresponds to the 11.8% weight of the incorporated polysulfone oligomer. In nitrogen, the onset of rapid weight loss began at ~500°C with only a 30% weight loss exhibited up to 800°C.

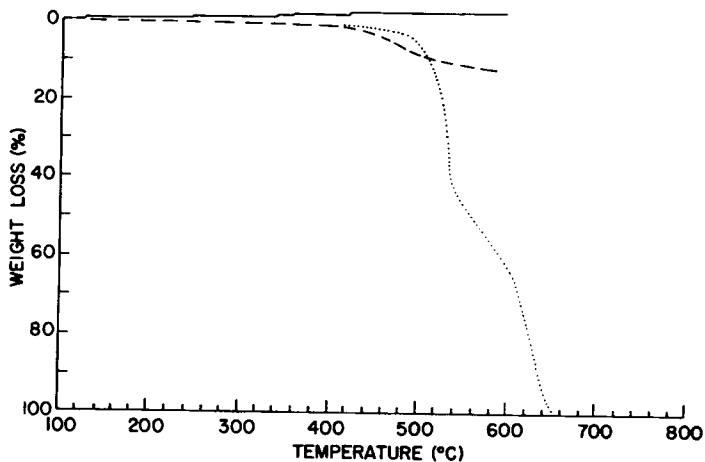


Fig. 4. Thermogravimetry of carboranesiloxane/polysulfone block copolymer in air: (---) block copolymer; (—) D_2 -*m*-carboranesiloxane; (···) polysulfone.

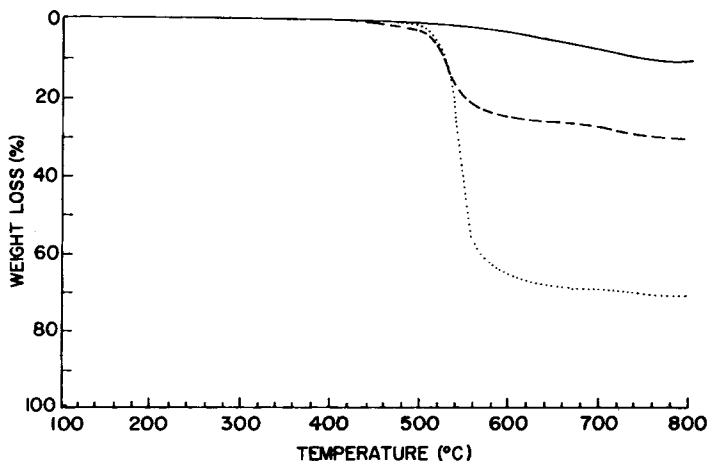


Fig. 5. Thermogravimetry of carboranesiloxane/polysulfone block copolymer in nitrogen: (---) block copolymer; (—) D_2 -*m*-carboranesiloxane; (···) polysulfone.

CONCLUSIONS

This work shows the versatility of bisureidosilanes in the preparation of carboranesiloxane-containing block copolymers and demonstrates the feasibility of preparing a host of carboranesiloxane-containing block copolymers. This work was the first reported synthesis of a carboranesiloxane-containing thermoplastic elastomer.

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