

Block Copolymerization of Unsaturated Monomers and Octamethylcyclotetrasiloxane*

MAURICE MORTON, A. A. REMBAUM,† and E. E. BOSTICK,‡
Institute of Rubber Research, University of Akron, Akron, Ohio

Synopsis

A study has been carried out on the preparation of block copolymers of styrene-dimethylsiloxane and isoprene-dimethylsiloxane. This has been accomplished by means of anionic polymerization, using potassium metal or potassium naphthalene as initiator, in tetrahydrofuran. Block copolymers of the ABA type were synthesized by first preparing the polystyrene or polyisoprene dianion, followed by polymerization of the octamethylcyclotetrasiloxane. Proof of the presence of these block copolymers was obtained from their solubility behavior and from the ability of the isoprene-siloxane polymers to undergo vulcanization by sulfur. The chain length of the polymeric blocks could be controlled in a predictable fashion, leading to a central segment (B) of polystyrene or polyisoprene, having a narrow molecular weight distribution, and two end segments (A) of polydimethylsiloxane, having a most probable distribution. The reverse type of block copolymer was not possible due to the inability of the siloxane to initiate styrene or isoprene polymerization.

INTRODUCTION

In a previous publication¹ it had been shown that octamethylcyclotetrasiloxane (D_4) could be rapidly converted to a long chain polysiloxane at room temperature by potassium naphthalene in tetrahydrofuran solvent. It was also shown that, under conditions of rigorous exclusion of impurities, two molecules of potassium naphthalene are required for the initiation of each polymer chain, which occurs by direct anionic attack on the cyclic monomer.

The ability of the naphthalene radical-anion to open the cyclic siloxane ring suggested the possibility of similar action by other carbanionic species. Since the alkali naphthalene complexes are known to initiate the polymerization of unsaturated monomers, such as styrene, butadiene, etc., these systems were thought capable of leading to a block copolymerization of such monomers and the D_4 . This paper describes the results of such

* Presented, in part, at the 133rd Meeting, American Chemical Society, San Francisco, March 1958. Taken, in part, from the Ph.D. Dissertation of E. E. Bostick, University of Akron, 1959.

† Present address: Jet Propulsion Laboratory, California Institute of Technology, Pasadena, Calif.

‡ Present address: Research Laboratory, General Electric Co., Schenectady, N. Y.

block copolymerizations, involving styrene and isoprene as the unsaturated monomers, and potassium naphthalene as the initiator.

EXPERIMENTAL

Materials

Some of the materials used in this work have already been described previously.¹ Additional materials are described below.

Decamethyltetrasiloxane. Decamethyltetrasiloxane, MD₂M, was distilled before use; Boiling point, 194°C. at 760 mm. Hg pressure.

Isoprene. Isoprene, (Phillips 99 mole-%), was placed over fresh sodium lumps, thoroughly degassed, and flash-distilled three times from sodium mirrors formed in a high vacuum. The first and last portions of each distillation were discarded. The final distillate ($n_D^{20} = 1.4216$) was divided into ampules fitted with breakable seals and sealed off under high vacuum (10^{-6} mm. Hg pressure). The ampules were stored at 0°C. until used.

Styrene. Styrene (Dow Chemical Company) was placed over finely ground calcium hydride, thoroughly degassed and redistilled into a clean flask. The first and last portions of the distillate were discarded. The portion of styrene collected was flash-distilled into ampules fitted with Eck and Krebs breakable seals and sealed off with a gas-oxygen torch under high vacuum. The styrene ampules were stored at 0°C. until ready for use.

Dimethyldichlorosilane. Dimethyldichlorosilane (Peninsular) was redistilled, b.p. 70°C. at 760 mm. Hg pressure before use.

Butanone. Butanone (Matheson, Coleman and Bell) was used as received.

Procedures

Block Polymerization

The individual procedures used in the preparation of the block copolymers described in this paper are included in the Results section. However, the general procedure is described below.

The experimental apparatus was similar to that used for the potassium naphthalene polymerizations previously described,¹ except that an additional ampule, containing the desired amount of freshly distilled, degassed styrene or isoprene, was attached. The procedure was to introduce styrene (or isoprene) to the potassium naphthalene solution before adding the siloxane tetramer. When the styrene (or isoprene) was transferred to the complex, there was an instantaneous color change from green to red. When the siloxane tetramer was added, only a dilution of color was immediately noticed. After a 30–40 min. induction period, the red styrene anion color began to fade considerably. Polymerization was evident from viscosity increase of the system.

After 12 hr., the polymer solution was very viscous, slightly translucent,

and very pale pink in color. Termination was carried out with methyl iodide, after which the polymer was processed in the usual manner.

Characterization of Block Copolymers

Two methods were employed in characterizing the block copolymers. Both were designed primarily for the detection of homopolymer.

One was the use of selective solvents to effect precipitation of polymer solutions. The other involved formation of a network by sulfur vulcanization, followed by solvent extraction.

Precipitation of Polymer Solutions. For *poly(styrene-dimethylsiloxane)*, the technique utilized was very similar to that of Morton and Nicholls,² except that precipitation distribution functions were not derived or plotted. The procedure involved the incremental addition of nonsolvent to dilute solutions of polymer. The polymer precipitated as the amount of nonsolvent increased, forming a two-phase system. The bottom layer was rich in polymer while the top layer was poor in polymer. After equilibrium was established, an aliquot of the supernatant layer was carefully removed and the dissolved polymer was determined by drying and weighing the solid residue. Individual samples were used for different amounts of nonsolvent, keeping the total volume constant. In this way, a relationship between dissolved polymer and per cent nonsolvent was obtained.

The first solvent-nonsolvent system used was benzene-methanol. Smooth curves were obtained for both block copolymer and mechanical mixtures of polystyrene and polydimethylsiloxane identical in composition. Since homopolymer could not be detected, this system was abandoned.

Next, a search was made for a material that would be a good solvent for one of the polymers and a poor solvent for the other. Decamethyltetrasiloxane was found to be a good solvent for polydimethylsiloxane and a nonsolvent for polystyrene at 27°C. This material was then used as a precipitant for both block copolymer and mechanical mixtures of polystyrene and polydimethylsiloxane dissolved in benzene. Positive differences between the block copolymer solution and the "control" solution were noticed. The block copolymer tended to form a turbid solution requiring centrifuging to effect phase separation, while the mixture was more easily separated.

For *poly(isoprene-dimethylsiloxane)*, a search for a proper system for differentiating between the block copolymer and polyisoprene/polydimethylsiloxane mixture resulted in the selection of butanone as a solvent at 50°C. and methanol as a nonsolvent. The polyisoprene homopolymer was found to dissolve in butanone at 50°C. and to precipitate as the temperature was lowered to 48°C. Polydimethylsiloxane was found to be soluble from 20°C. to 50°C.

By using a procedure similar to that described previously for styrene-dimethylsiloxane polymeric systems, proof of block was established for the isoprene-dimethylsiloxane polymeric systems.

RESULTS AND DISCUSSION

Styrene-Dimethylsiloxane Block Copolymers

Potassium Metal Initiation. Tetrahydrofuran (200 ml., 2.44 mole) was distilled into a flask containing a potassium metal mirror formed *in vacuo*. Styrene (8.4 g., 80.7 mmole) was added dropwise with stirring at -80°C . An instantaneous polymerization occurred which produced a dark red solution. The solution was filtered through a medium porosity fritted glass disk into a receiving flask. The solution was then divided into two portions. One portion was terminated with water, precipitated in methanol, and dried at 70°C . and 1 mm. Hg pressure. The yield was found to be 5.1 g. of polystyrene with a calculated number-average molecular weight of 160,000.

The second portion, containing 3.3 g. of polystyrene with active anion chain ends, was transferred under vacuum (10^{-6} mm. Hg) to a flask containing 120 ml. of anhydrous, degassed tetrahydrofuran and fitted with an ampule of 5.4 g. (0.018 mole) of siloxane tetramer. The siloxane tetramer was mixed thoroughly with the polystyrene solution by magnetic stirring. The apparatus was fitted to the vacuum line and 190 ml. of the tetrahydrofuran was distilled off. The red color of the styrene anion faded to a translucent pale pink as the solvent was being distilled off. The viscosity of the reaction mixture increased sharply. After 12 hr., the reaction mixture was a viscous opaque mass with a very slight pink color.

Methyl iodide was used to terminate the reaction, as evidenced by the disappearance of the pink color. The solution was diluted with tetrahydrofuran and precipitated in excess methanol. The resulting polymer was dried at 70°C . and 1 mm. Hg. The yield was 6.6 g. of white, resinous polymer. Based on a material balance, the polymer contained 50% polystyrene and 50% polydimethylsiloxane segments by weight.

Potassium Naphthalene Initiation. Styrene monomer (6.3 g., 60.6 mmoles) was added dropwise with stirring at -80°C . to 100 ml. (1.22 mole) tetrahydrofuran containing 0.24 mmole of potassium naphthalene complex. An instantaneous polymerization accompanied by a color change from green to red was noted. The resulting polymer solution was divided into two portions. One portion was terminated with water, precipitated in methanol and vacuum-dried at 70°C . The yield was 3.9 g. of polystyrene with a calculated number-average molecular weight of 56,000.

The other portion was mixed with 64 g. (0.865 mole) of octamethylcyclotetrasiloxane in 250 ml. (3.056 mole) of tetrahydrofuran. After thorough mixing, 180 ml. of tetrahydrofuran was removed by means of the vacuum line. Polymerization proceeded with a change in color from red to pale pink. After 16 hr., the solution was a viscous, opaque mass.

Methyl iodide (1 ml.) was used for termination. When termination was considered to be complete, the flask was opened and the polymer solution precipitated in methanol. The resulting polymer was 42.1 g. of a viscous, opaque gum. Based on a material balance, the block copolymer consisted of 5.7% by weight polystyrene and 92.3% by weight polydimethylsiloxane.

In order to check the stoichiometry of these block copolymerizations, some experiments were conducted along the lines described above, except that only enough styrene was used to react with all the potassium naphthalene. In this way, the "block copolymer" had only a very small proportion of styrene, and could be characterized, for molecular weight purposes, as a polydimethylsiloxane. Data on these polymers are shown in Table I, where the measured viscosity-average molecular weights (\bar{M}_v) were transformed to their number-average (\bar{M}_n) values by means of Flory's relation³ for a polymer having the most probable molecular weight distribution. The \bar{M}_v values were obtained from intrinsic viscosities by using the equation of Flory et al.⁴ for this system. It can be seen that the measured and predicted values of \bar{M}_n agree quite well, indicating a stoichiometry of two initiator molecules per chain, as expected.

TABLE I
Polymerization of D₄ by Styrene Dianions

[Initiator] × 10 ⁴				\bar{M}_n (theor.)
[D]	$[\eta]_{\text{MEK}}^{30}$	$\bar{M}_v \times 10^{-5}$	$\bar{M}_v/1.79 \times 10^{-5}$	× 10 ^{-5a}
2.9	0.86	8.2	4.8	5.1
3.6	0.78	6.9	3.8	4.1

^a \bar{M}_n (theor.) = g. D^{1/2} [Initiator].

Next, larger quantities of styrene were polymerized and D₄ subsequently added to form an A-B-A block copolymer with polydimethylsiloxane ends and a polystyrene center. Table II lists the characteristics of the resulting block copolymer. It is interesting to note that, in these systems, there was a persistence of a very pale pink color until the "terminator" was added. This can be explained on the basis of the siloxane equilibration, which would be expected to include an equilibrium amount of the red styrene anion.

TABLE II
Polysiloxane-Polystyrene-Polysiloxane Block Copolymers^a

Polystyrene segment		Polysiloxane segment		Characteristics
\bar{M}_n (calc.) × 10 ⁻⁵	Wt.-%	\bar{M}_n (calc.) × 10 ⁻⁵	Wt.-%	
0.56	5.7	4.65	94.3	Soft white gum
1.6	50	0.8	50	White resin

^a Structure: A-B-A, where A = polysiloxane, B = polystyrene.

Efforts to characterize the block copolymers were made using a selective solvent-nonsolvent system. The solvent used was benzene and the nonsolvent, decamethyltetrasiloxane (i.e., MD₂M, in dimethylsiloxane nomenclature). Incremental additions of nonsolvent to dilute benzene solutions of polymer resulted in the precipitation curves shown in Figure 1.

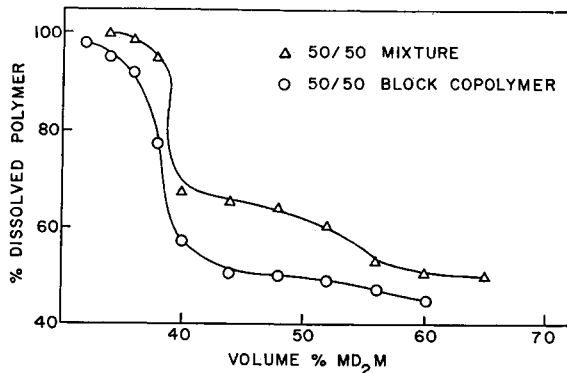


Fig. 1. Precipitation curves for polystyrene/polydimethylsiloxane solutions in benzene at 27°C.

The precipitation curve of a 50/50 mechanical mixture of polystyrene and polydimethylsiloxane approached a limit of 50% polymer since MD₂M is a solvent for silicone polymers and a nonsolvent for polystyrene at 27°C. The block copolymer solutions were also found to develop a persistent turbidity which required centrifuging for phase separation. The precipitation curve for the block copolymer was found to be continuous and to go below the 50% limit of possible polydimethylsiloxane content. Hence it is obvious that a block copolymer was present, although some free polysiloxane may also have been present due to the nature of the equilibration process.

Isoprene-Dimethylsiloxane Block Copolymers

Potassium Metal Initiation. Anhydrous degassed isoprene (41.2 g. 0.605 mole) was added dropwise with stirring at -80°C. to 240 ml. (2.93 mole) tetrahydrofuran in a flask containing a potassium metal mirror formed by sublimation at 10⁻⁶ mm. Hg pressure. A brownish-red color developed immediately, and polymerization was rapid. After 2 hr., the polymer solution was transferred through a fritted disk into two flasks. One portion was terminated with water, precipitated in methanol, and vacuum-dried. The yield was 25.6 grams of polyisoprene with a number-average molecular weight of 66,000.

The other portion was mixed *in vacuo* with 47.5 g. (0.16 mole) of octamethylcyclotetrasiloxane. After stirring for several hours, 125 ml. of tetrahydrofuran was removed by means of the vacuum line. Polymerization continued with a visible color transition, brownish-red to opaque white, and a sharp viscosity increase. After 24 hr. reaction time, anhydrous degassed methyl iodide was used to terminate the reaction. The polymer was precipitated in methanol containing phenyl-β-naphthylamine and Dry Ice, vacuum-dried at room temperature, and stored under CO₂. The yield was 51.2 g. of block copolymer. Based on the polyisoprene material balance, the block copolymer consisted of 30.5% polyisoprene segments and 69.5%

polydimethylsiloxane segments. The block copolymer was a viscous opaque white gum.

Potassium Naphthalene Initiator. Anhydrous degassed isoprene (40 g., 0.588 mole) was added dropwise with stirring at $-80^{\circ}\text{C}.$ to 240 ml. (2.93 mole) of tetrahydrofuran containing 0.267 mmole of potassium naphthalene complex. An instantaneous color change from dark green to brownish-red was accompanied by polymerization. The polymer solution was then divided into two portions. One portion was found to contain 17.7 g. of polyisoprene with a calculated number-average molecular weight of 300,000.

The other portion was mixed with 12 g. (40.5 mmole) of octamethylcyclotetrasiloxane and a total of 150 ml. of tetrahydrofuran. After thorough mixing, 100 ml. of tetrahydrofuran was removed to the vacuum reservoir. Polymerization was, as described previously, accompanied by a sharp viscosity increase and a color change from brownish-red to opaque white.

After 24 hr., the reaction was neutralized with methyl iodide and the polymer recovered as described for the potassium metal experiment.

The yield was found to be 30.5 g. of an elastic block copolymer. With polyisoprene as a basis, the composition of the block copolymer was calculated to be 73% polyisoprene segments by weight and 27% polydimethylsiloxane segments by weight.

Since rubbery products were formed, several siloxane-isoprene-siloxane block copolymers were prepared with some variations in composition. The characteristics of the resulting polymers are listed in Table III.

TABLE III
Polysiloxane-Polyisoprene-Polysiloxane Block Copolymers^a

Isoprene segment		Siloxane segment		Characteristics
$\bar{M}_n(\text{calc.})$ $\times 10^{-5}$	Wt.-%	$\bar{M}_n(\text{calc.})$ $\times 10^{-5}$	Wt.-%	
0.5	52	0.25	48	White, tacky, viscous fluid
0.66	30.5	1.5	69.5	Soft, white viscous fluid
1.5	15	4.25	85	Soft, white gum
3.0	30	3.5	70	Soft, crumbly white gum
3.0	73	1.2	27	Rubbery white gum

^a Structure: A—B—A, where A = polydimethylsiloxane, B = polyisoprene.

It can be observed from these results that the rubbery properties of the block copolymer were found to increase as the molecular weight of the isoprene segment increased or the siloxane content decreased. The elastic properties of the block copolymers were found to be a composite of the properties of the homopolymers. These copolymers were characterized by two methods. One involved selective solvent precipitation and the other consisted of the preparation of a sulfur vulcanizate followed by extraction.

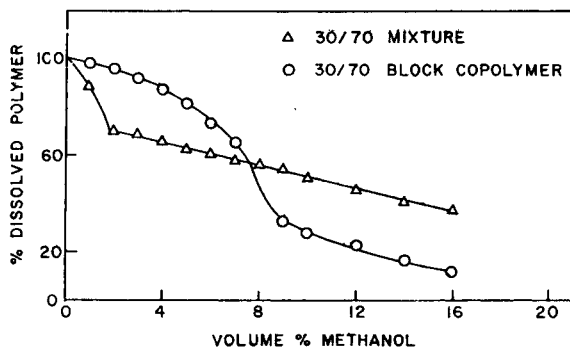


Fig. 2. Precipitation curves for polystyrene/polydimethylsiloxane solutions in methyl ethyl ketone at 50°C.

The precipitation curves of the 30/70 block copolymer in a butanone-methanol system at 50°C. are shown in Figure 2.

Butanone is a poor solvent for polyisoprene and a good solvent for polydimethylsiloxane at 50°C. Consequently, a sharp inflection point at the 70% dissolved polymer level was found for the mechanical mixture, while the curve for the block copolymer was smooth and continuous as the concentration of nonsolvent was increased. Neither curve was found to approach a limiting value, but the difference in shape of the two curves is considered to be significant.

By preparing a sulfur vulcanizate of a block copolymer of isoprene and dimethylsiloxane and extracting with benzene, any homopolymer of dimethylsiloxane should be removed. This was done with a block copolymer composed of 70% by weight polyisoprene and 30% by weight polydimethylsiloxane. Extraction for 24 and 48 hr. with cold benzene yielded only traces of a tacky gum which appeared to be block copolymer. Even though some chain scission may occur to produce homopolymeric segments of dimethylsiloxane, this reaction appears to have been only a minor effect. Based on the precipitation and extraction results, these polymers are apparently all block copolymers of siloxane-isoprene-siloxane segments.

Chain Extension of Block Copolymers

If the isoprene-siloxane block copolymer is considered at equilibrium, there should be active silanolate anions at each end of the chains:



If all of the chains are active, then the A—B—A block copolymer may be coupled, or extended to produce a higher molecular weight . . . A—B—A—A—B—A . . . block copolymer. Dimethyldichlorosilane was selected and used in a chain extension experiment. The reaction that was expected to occur was the hydrolysis of the chloro groups by the basic potassium silanolate chain terminals.

An experiment was conducted to increase the chain length of the block copolymers prepared with polyisoprene centers and polydimethylsiloxane ends. The approach used was to add a dichlorodialkylsilane to a block copolymer before terminating with methyl iodide. The potassium silanolate chain ends were considered to be basic enough in tetrahydrofuran to hydrolyze the chloro groups, thereby linking at least two chains together.

Anhydrous, degassed isoprene (30 g., 0.441 mole) was added with stirring to 0.749 mmole of potassium naphthalene catalyst dissolved in 35 ml. of anhydrous, degassed tetrahydrofuran. After polymerization was finished (1 hr., 0°C.), 24 g. (0.081 mole) of anhydrous, degassed D₄ was added and thoroughly mixed with the "active" polymer solution.

After polymerization for 12 hr. at room temperature, the polymer solution was divided. One portion was terminated with methyl iodide, coagulated in methanol, and vacuum-dried at 60°C. The composition of this block copolymer was found to be 70% polyisoprene and 30% polysiloxane by weight. The intrinsic viscosity of this block copolymer, measured in benzene at 30°C., was found to be 0.375. The yield of this portion was found to be 10 g.

Dimethyldichlorosilane (0.30 mmole) was added to the remaining portion. A significant increase in the viscosity of the reaction mixture was noted. After 4 hr. reaction time, methyl iodide was added to terminate residual silanolate chain ends, if present. The yield of dry polymer from this portion was found to be 30 g. Intrinsic viscosity of the polymer was found to be 0.495 in benzene at 30°C. This corresponds to a doubling of the molecular weight.

Vulcanization of Block Copolymers

Good evidence for the presence of a block copolymer of the poly(isoprene-dimethylsiloxane) type would be its susceptibility to vulcanization into a network, especially by means of sulfur systems, since polysiloxanes do not crosslink under these conditions. At the same time, such networks would be of interest for examination of elastomeric properties.

For this purpose, the following compounding recipe was used: poly(isoprene-dimethylsiloxane)(30/70), 100 parts; hydrated silica (Dupont Valron Estersil), 45 parts; sulfur, 3 parts; benzothiazolyl disulfide (MBTS), 1.25 parts; and diphenylguanidine, 0.25 parts. The ingredients were mixed on a mill and vulcanized in a press mold for 30 min. at 150°C. The resulting vulcanizate was insoluble in benzene, yielding only traces of a tacky gum. Hence it appeared to be essentially a block copolymer. Furthermore it exhibited a tensile strength of 1200 psi and an ultimate elongation of 750%.

It is also interesting to note that a 73/27 poly(isoprene-dimethylsiloxane), when compounded and vulcanized without any reinforcing silica filler, using the above recipe, also showed a tensile strength of 1250 psi and an ultimate elongation of 700%. This differs sharply from the behavior of polydimethylsiloxanes, which show no measurable tensile properties in the gum vulcanizate form.

It should be added that, in addition to the above results on sulfur vulcanization, it has also been found possible to crosslink these block copolymers with peroxides, under relatively mild conditions.⁵

This research work was supported by a grant from the National Science Foundation, G-2630.

References

1. Morton, M., and E. E. Bostick, *J. Polymer Sci.*, **A2**, 523 (1964).
2. Morton, M., and R. V. V. Nicholls, *Can. J. Res.*, **B25**, 150 (1947).
3. Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953, p. 313.
4. Flory, P. J., L. Mandelkern, J. B. Kinsinger, and W. B. Schultz, *J. Am. Chem. Soc.*, **74**, 3364 (1952).
5. Morton, M., and A. Rembaum, U. S. Pat. 3,051,684 (Aug. 28, 1962).

Résumé

On a étudié la préparation de copolymères à blocs styrène-diméthylsiloxane et isoprène-diméthylsiloxane. Ceci a été fait par polymérisation anionique en employant le potassium métallique ou le naphthalène potassium comme initiateur dans le tétrahydrofuranne. On a synthétisé des copolymères à blocs du type ABA en préparant d'abord le polystyrène ou le polyisoprène dianion suivi de la polymérisation de l'octaméthylcyclotétrasiloxane. On a obtenu la preuve de la présence des ces copolymères à blocs par leurs propriétés de solubilité et par l'aptitude des polymères isoprène-siloxane à subir une vulcanisation au soufre. On peut contrôler a priori la longueur des blocs polymériques, conduisant à un segment central (B) de polystyrène ou de polyisoprène, ayant une distribution de poids moléculaire étroite et à deux segments terminaux (A) de polydiméthylsiloxane ayant une distribution plus probable. Un type inverse de copolymère à blocs n'est pas possible, étant donné l'inaptitude du siloxane d'initier la polymérisation du styrène ou de l'isoprène.

Zusammenfassung

Eine Untersuchung der Herstellung von Blockcopolymeren aus Styrol-Dimethylsiloxan und Isopren-Dimethylsiloxan wurde durchgeführt. Diese wurde durch anionische Polymerisation unter Verwendung von Kaliummetall oder Kaliumnaphthalin als Starter in Tetrahydrofuran erreicht. Blockcopolymeren von ABA-Typ wurden durch Herstellung des Polystyrol- oder Polyisoprendianions und darauffolgender Polymerisation des Oktamethylcyclotetrasiloxan dargestellt. Der Beweis der Anwesenheit dieser Blockpolymeren wurde durch ihr Löslichkeitsverhalten und aus der Fähigkeit des Isopren-Siloxanpolymeren zur Schwefelvulkanisation erbracht. Die Kettenlänge der Polymerblocks konnte im voraus festgelegt werden und ergab ein Polystyrol- oder Polyisoprenzentralsegment (B) mit enger Molekulargewichtsverteilung und zwei Polydimethylsiloxanendsegmente (A) mit der "wahrscheinlichen" Verteilung. Der umgekehrte Blockpolymertyp war wegen der Unfähigkeit von Siloxan zur Styrol- oder Isoprenpolymerisationsstartung nicht herstellbar.

Received November 26, 1963