# Synthesis and Characterization of Poly(hexamethylene sebacate)–Poly(dimethylsiloxane) Block Copolymers

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*Received July 25, 1977*

ABSTRACT: The synthesis and characterization of a series of poly(hexamethylene sebacate) (HMS)–poly(dimethylsiloxane) (DMS) multiblock copolymers is described. The copolymers were prepared by endwise coupling chloro- or dimethylamino-terminated DMS with hydroxyl-terminated HMS and alternating structures of the (HMS–DMS)$_n$ type resulted. Copolymers ranging in composition from 19 to 90 wt % DMS were synthesized and characterized by NMR, viscometry, GPC, DSC, and microscopy techniques. All of the copolymers were found to crystallize.

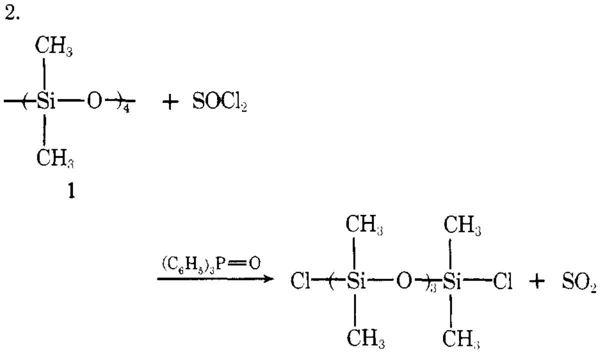
This is the first in a forthcoming series of papers describing the synthesis and physical properties of block copolymers composed of poly(hexamethylene sebacate) (HMS) and poly(dimethylsiloxane) (DMS). These copolymers have alternating blocks of HMS and DMS along the copolymer chain, and they have been prepared by condensation reactions involving preformed, functionally terminated, polymeric segments. In this regard, they are more akin to other reported well-defined polyester–siloxane block copolymers than to the well-known bisphenol-A polycarbonate–DMS copolymers.[1-3] In this study, we have used chloro- and dimethylamino-terminated siloxanes to prepare the copolymers, and we have used HMS, a highly crystalline polyester melting near 67 °C, as the hard block rather than the high transition temperature aromatic or alicyclic polyester hard blocks previously described.[1]

Our motivation for this study was our interest in comparing the properties of these (HMS–DMS)$_n$ copolymers with our previously synthesized (HMS–MEPS)$_n$ block copolymers,[4,5] where MEPS is poly(2-methyl-2-ethyl-1,3-propylene sebacate), an amorphous isomer of HMS. In the latter system, the block components are quite similar whereas in the siloxane copolymers, the components are very dissimilar and are expected to be incompatible with each other. The differences in these systems are reflected, in part, in their rheological and solid state properties.[6] In this paper the synthesis of (HMS–DMS)$_n$ copolymers covering a wide compositional range will be discussed in detail and some more general remarks will be made about their physical properties.

## Experimental Section

**Hydroxyl-Terminated Poly(hexamethylene sebacate).** Poly(hexamethylene sebacate) (HMS) was prepared in high yields by the acid-catalyzed melt condensation of sebacic acid with 1,6-hexanediol.[7] Excess diol was used to maintain hydroxyl termination and to control the molecular weight.

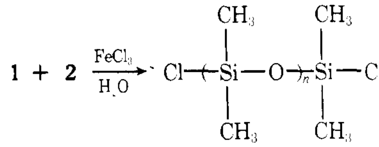
**Chloro-Terminated Poly(dimethylsiloxanes).** These materials were synthesized according to the two-stage process shown in eq 1 and 2.



$$\underset{\mathbf{1}}{(\text{Si}(CH_3)_2\text{—O})_4} + SOCl_2 \xrightarrow{(C_6H_5)_3P=O} \underset{\mathbf{2}}{Cl\text{—}(\text{Si}(CH_3)_2\text{—O})_3\text{—Si}(CH_3)_2\text{—Cl}} + SO_2 \quad (1)$$

1

2

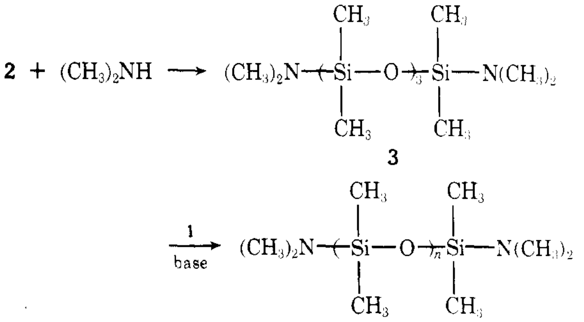


$$1 + 2 \xrightarrow[H_2O]{FeCl_3} Cl\text{—}(\text{Si}(CH_3)_2\text{—O})_n\text{—Si}(CH_3)_2\text{—Cl} \quad (2)$$

Octamethylcyclotetrasiloxane (1) and thionyl chloride in the presence of a small amount of triphenylphosphine oxide were used to prepare 1,7-dichlorooctamethyltetrasiloxane (2) according to the method of Bennett.[8] The product was isolated by distillation at 20 Torr of pressure (bp 105–110 °C (lit.[8] 115 °C)) and gave a satisfactory elemental analysis.

Higher molecular weight chloro-terminated siloxanes were prepared according to eq 2. In a typical synthesis, 1 (0.5 mol) and 2 (0.05 mol) were combined with ferric chloride (0.006 mol) and heated at 75 °C overnight after adding one drop of water to initiate the reaction. Afterwards, the reaction vessel was transferred to a nitrogen-filled drybox and 5 g of dry, activated charcoal was added and the slurry was stirred overnight at room temperature. Celite filter aid (25 g) was then added and the reaction mixture was filtered in the drybox through a coarse fritted glass funnel. The filtrate was collected and sparged with argon for 1 h while heating to 185 °C. This removed the oligomeric, low-boiling siloxanes and left the desired, chloro-terminated, linear DMS fluid which was stored in a desiccator until used. A polymer prepared according to the above procedure contains about 3% chlorine and has a number average molecular weight ($\overline{M}_n$) near 2300 g/mol. Control of the final molecular weight is achieved by adjusting the initial ratio of cyclic tetramer to linear prepolymer.

**Dimethylamino-Terminated Poly(dimethylsiloxanes).** These materials were synthesized according to the processes described in eq 1 and 3.



$$2 + (CH_3)_2NH \longrightarrow \underset{\mathbf{3}}{(CH_3)_2N\text{—}(\text{Si}(CH_3)_2\text{—O})_3\text{—Si}(CH_3)_2\text{—N}(CH_3)_2}$$

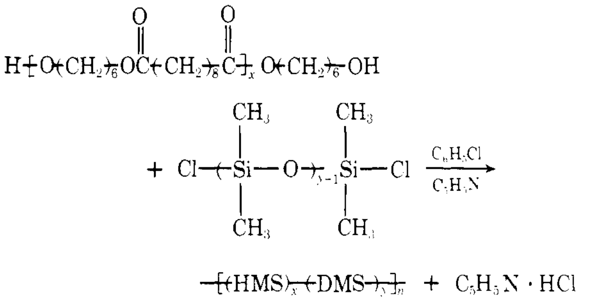
3

$$\xrightarrow[\text{base}]{1} (CH_3)_2N\text{—}(\text{Si}(CH_3)_2\text{—O})_n\text{—Si}(CH_3)_2\text{—N}(CH_3)_2 \quad (3)$$

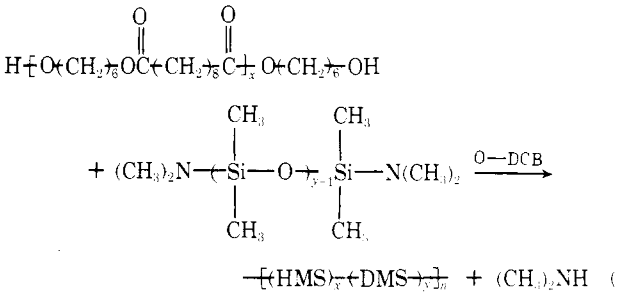
1,7-Bis(dimethylamino)octamethyltetrasiloxane (3) was prepared according to the method of Creamer[9] by reacting dry dimethylamine with 2 in the presence of magnesium as an HCl scavenger. A 59% yield of 3 boiling at 126–128 °C and 22 Torr of pressure was obtained, and it gave a satisfactory elemental analysis.

Higher molecular weight dimethylamino-terminated siloxanes were prepared according to eq 3. In a typical synthesis 1 (0.27 mol) and 3 (0.022 mol) were combined and purged with nitrogen at 90–95 °C for 15 min before adding 0.98 g of the equilibrium polymerization catalyst, tetramethylammonium silanolate.[10] The polymerization was run for 5 h at 90–95 °C and then the catalyst was destroyed by vigorous nitrogen purging for 2 h at 140 °C. The nitrogen content determined by potentiometric end group titration was 0.65% which corresponded to a $\overline{M}_n$ of 4310. The molecular weights of other siloxane samples were controlled by varying the ratio of 1 and 3.

**Block Copolymer Synthesis.** The alternating block copolymers of HMS and DMS were prepared by coupling reactions involving the terminal hydroxyl groups on HMS and either the chloro- or dimethylaminosilyl-terminal groups on DMS. These two copolymerization processes are shown in eq 4 and 5.



$$\mathrm{H{+}\!\left[O(CH_2)_6O\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}\right]_x O(CH_2)_6OH} + \mathrm{Cl{-}\!\left(\underset{CH_3}{\overset{CH_3}{Si}}{-}O\right)_{y-1}\underset{CH_3}{\overset{CH_3}{Si}}{-}Cl} \xrightarrow[C_5H_5N]{C_6H_5Cl} \mathrm{-\!\left[(HMS)_x(DMS)_y\right]_n} + \mathrm{C_5H_5N\cdot HCl} \quad (4)$$



$$\mathrm{H{+}\!\left[O(CH_2)_6O\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}\right]_x O(CH_2)_6OH} + \mathrm{(CH_3)_2N{-}\!\left(\underset{CH_3}{\overset{CH_3}{Si}}{-}O\right)_{y-1}\underset{CH_3}{\overset{CH_3}{Si}}{-}N(CH_3)_2} \xrightarrow{O-DCB} \mathrm{-\!\left[(HMS)_x(DMS)_y\right]_n} + \mathrm{(CH_3)_2NH} \quad (5)$$

According to eq 4, HMS (15.3 g, 5 × $10^{-3}$ mol) and chloro-terminated DMS fluid (22.1 g, 5 × $10^{-3}$ mol) were heated to reflux in chlorobenzene (150 mL) and then pyridine (5 mL) was added. Refluxing was continued for 4 h and then the cooled reaction mixture was added to a tenfold excess of methanol and the precipitate was isolated by filtration. The product was reprecipitated twice from tetrahydrofuran into methanol and finally dried in vacuo. A yield of 28.4 g or 75% was realized from this typical coupling reaction. The block copolymer was analyzed by NMR to contain 42.8 wt % HMS and 57.2 wt % DMS, and it had an intrinsic viscosity in chloroform of 0.91 dL/g at 25 °C.

A typical reaction carried out according to eq 5 is described below. To a solution of dimethylamino-terminated DMS (87 g, 0.02 mol) in *o*-dichlorobenzene (*o*-DCB) (45 mL) was added one-half of a solution of HMS (53 g, 0.02 mol) in *o*-dichlorobenzene (36 mL). The reaction mixture was maintained at 150–160 °C with a nitrogen purge for 12 h, after which one-quarter of the HMS solution was added. Increments of one-eight of the HMS solution were added to the reaction mixture after 15 and 16 h of reaction, respectively, and the reaction was terminated after 20 h. The block copolymer workup was similar to that described above, and the yield was 87%. The block copolymer contained 52 wt % DMS by NMR analysis, and it had a $\overline{M}_n$ of 20 800 determined from membrane osmometry in toluene at 36 °C.

**Physical Methods.** Proton magnetic resonance spectra were measured at 25 °C with a JEOLCO 60-MHz spectrometer, and they were used to determine the composition of the copolymers. Deuteriochloroform (without added tetramethylsilane) was used as solvent and the proton signals arising from the methyl protons in the DMS blocks ($\delta$ 0 ppm) were easily distinguished from the proton signals ($\delta$ 1.3, 2.3, and 3.9 ppm) emanating from the HMS blocks.[7] A typical NMR spectrum is shown in Figure 1 for a block copolymer containing 27 wt % DMS.

Intrinsic viscosities and gel permeation chromatograms were obtained using chloroform as solvent at 25 °C. Cannon-Ubbelohde viscometers were used for the former measurements and a Waters Model 200 gel permeation chromatograph (GPC) with four linear $10^5$ Å Styragel columns and a flow rate of 1 mL/min was used for the chromatography work. Monodisperse polystyrenes from Pressure Chemical Co. were used to calibrate the columns. Number average molecular weights were determined by DeBell and Richardson Co., using membrane osmometry with toluene solvent at 36 °C.

A Perkin-Elmer Model 1-B differential scanning calorimeter (DSC) was used to establish crystallinity in the polymers and to determine thermal transition temperatures. A temperature scan rate of 10 °C/min was used for all the measurements. Data for crystallization were obtained by cooling the samples from the melt at 10 °C/min in the calorimeter and recording the temperature at which the exothermic transition reached a maximum on the thermogram. The melting temperature data were recorded in an analogous manner using the endothermic transition and a 10 °C/min heating rate.

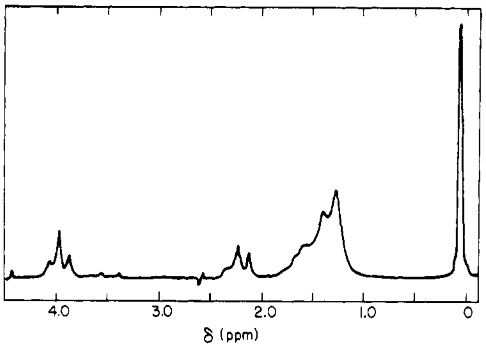


**Figure 1.** NMR spectrum of HMS–DMS block copolymer containing 27 wt % DMS.

### Table I
### Synthesis and Characterization Data for HMS–DMS Block Copolymers

| Sample[a] | Block $\overline{M}_n \times 10^{-3}$ (HMS) | (DMS) | Yield, % | Wt % DMS in copolym | $[n]$, dL/g | MWD (GPC) |
|---|---|---|---|---|---|---|
| HMS | 3.2 | | | 0 | 0.21 | 1.52 |
| HMS | 3.5 | | | 0 | 0.23 | 1.88 |
| A | 3.2 | 1.2 | 74.5 | 19.1 | 0.33 | 1.76 |
| B | 3.2 | 1.4 | 87.0 | 27.0 | 0.61 | 2.15 |
| C | 3.2 | 1.4 | | 26.1 | 0.42 | |
| D | 3.5 | 2.3 | 91.0 | 36.5 | 0.49 | 2.03 |
| E | 3.2 | 2.3 | 81.5 | 41.7 | 0.84 | 2.58 |
| F | 3.2 | 2.3 | 87.2 | 42.8 | 0.25 | 1.51 |
| G | 3.5 | 4.6 | 87.5 | 49.5 | 0.48 | 1.95 |
| H | 3.2 | 4.6 | 76.0 | 57.2 | 0.91 | |
| I | 3.2 | 10.6 | 54.5 | 69.2 | 0.53 | 1.84 |
| J | 3.5 | 10.6 | 74.4 | 72.5 | 0.44 | |
| L[b] | 2.5 | 4.3 | 86.9 | 59.8 | 0.39 | |
| M[b] | 2.7 | 11.2 | 84.8 | 71.0 | 0.38 | |
| N[b,c] | 2.7 | 27.0 | 84.1 | 91.0 | 0.45 | |

[a] Copolymers A–J were prepared with chlorosiloxanes (eq 4) and copolymers L–N were prepared according to eq 5. [b] Number average molecular weights for samples L, M, and N are 20.8 × $10^3$, 25.1 × $10^3$, and 44 × $10^3$, respectively. [c] $[n]_i$ measured in THF at 25 °C.

## Results and Discussion

$(AB)_n$ type block copolymers covering a wide range of compositions were prepared by varying the molecular weight of the DMS over a wide range while keeping the HMS block length relatively constant. The HMS and DMS segments alternate regularly along the block copolymer chain because the reactive terminal groups on the two homopolymer segments are different and coupling reactions can only occur between dissimilar segments. The synthesis and characterization data for these $(HMS–DMS)_n$ block copolymers are shown in Table I.

In general, the copolymer yields, after several precipitations, are on the order of 75% or higher, and the experimentally determined copolymer compositions are close to those calculated from the relative molecular weights of the starting polymers.

The intrinsic viscosity data in Table I range from 0.21 dL/g for HMS homopolymer to 0.91 dL/g for block copolymer H. The magnitudes of the viscosities clearly indicate that coupling of the HMS and DMS segments occurred and that the desired block copolymers were formed. In the cases of copolymers L, M, and N, osmometry data confirm this notion and indicate that these samples have number average mo-

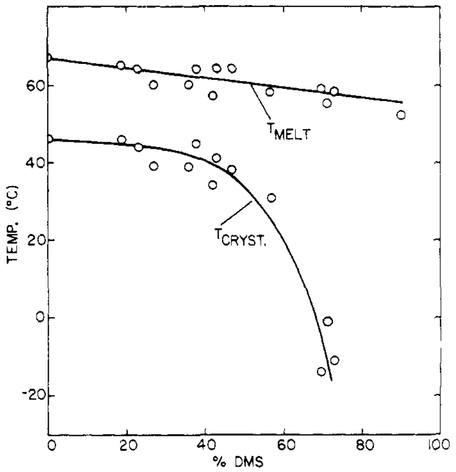


**Figure 2.** Melting and crystallization temperatures for HMS-DMS block copolymers.

lecular weights of $20.8 \times 10^3$, $25.1 \times 10^3$, and $44 \times 10^3$, respectively. A value of $n \simeq 2$ is calculated for these $(AB)_n$ type block copolymers and higher values of $n$ are anticipated for several of the other copolymers listed in Table I. Gel permeation chromatograms indicated that the copolymers had smaller elution volumes than HMS homopolymer, and there was no evidence of homopolymer contamination of the copolymers.

It is difficult, at this point, to make a general comparison of the two different copolymerization processes shown in eq 4 and 5 because the dimethylamino-terminated siloxane process (eq 5) was only tried in the synthesis of siloxane-rich copolymers. However, over the limited range of 57-72 wt % DMS where both procedures were used to make a total of five copolymers, the results show that the process utilizing dimethylamino-terminated siloxanes gives higher yields of copolymer product but that higher molecular weight copolymers are produced by the chlorosiloxane process described in eq 4.

The solid state properties of these multiblock copolymers will be discussed in detail elsewhere,[11] but it is appropriate to mention here some of their general characteristics. Each of the copolymers shows film-forming capability and, in general, as the siloxane content is increased, the samples become softer, less brittle, and more elastomeric, particularly at higher molecular weight. Copolymer films prepared by solvent and melt-casting procedures are opaque over the entire composition range, and they tend to remain opaque even in the melt, thus suggesting highly phase-separated structures for these block copolymers. Further evidence for phase separation has been provided by transmission electron microscopy on films cast from preferential solvents for HMS and DMS.

The copolymers shown in Table I demonstrate a remarkable ability to crystallize from the melt in a spherulitic texture over the entire copolymer composition range studied. Figure 2 shows the temperatures at which the copolymers crystallize when cooled from the melt at 10 °C/min and the temperatures at which they subsequently melt upon reheating at the same rate. Since the endothermic transition temperatures are in the vicinity of 60 °C, it is clear that HMS is the component forming the crystalline phase. The sharp decline in the exothermic transition temperatures as the siloxane content in the copolymers is increased reflects a decrease in crystallization rate similar to that observed in the $(HMS\text{-}MEPS)_n$ system[5] and, perhaps, even a change in nucleation mechanism akin to that observed in some polyethylene oxide systems.[12,13]

The surface characteristics of these copolymers are interesting because their wetting behavior is similar to DMS homopolymer.[6] Details of these investigations will be forthcoming in future publications.

**Acknowledgment.** The authors gratefully acknowledge the advice and assistance of R. Schank in preparing the siloxane prepolymers. We also thank A. Goedde for the NMR data, J. Pacco for the GPC data, and O. McFarland for the potentiometric titrations.

## References and Notes

(1) A. Noshay, M. Matzner and T. C. Williams, *Ind. Eng. Chem., Prod. Res. Dev.*, **12**, 268 (1973).
(2) T. J. Pacansky, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **17**, 564 (1976).
(3) H. A. Vaughn, *J. Polym. Sci., Part B*, **7**, 569 (1969).
(4) J. J. O'Malley, *J. Polym. Sci., Polym. Lett. Ed.*, **12**, 381 (1974).
(5) J. J. O'Malley, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 1353 (1975).
(6) J. J. O'Malley, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **18**, 226 (1977).
(7) J. J. O'Malley and W. J. Stauffer, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 865 (1974).
(8) E. W. Bennett, U.S. Patents 3 642 851 and 3 646 090 (1972).
(9) C. E. Creamer, U.S. Patent 3 467 686 (1969).
(10) M. Matzner, A. Noshay, and R. Barclay, U.S. Patent 3 701 815 (1972).
(11) J. J. O'Malley and W. J. Stauffer, *Polym. Eng. Sci.*, **17**, 510 (1977).
(12) F. P. Price, paper presented at the IUPAC Meeting, Wiesbaden, Germany, 1959.
(13) J. J. O'Malley, R. G. Crystal, and P. F. Erhardt, "Block Polymers", S. L. Aggarwal, Ed., Plenum Press, New York, N.Y., 1970, p 163.