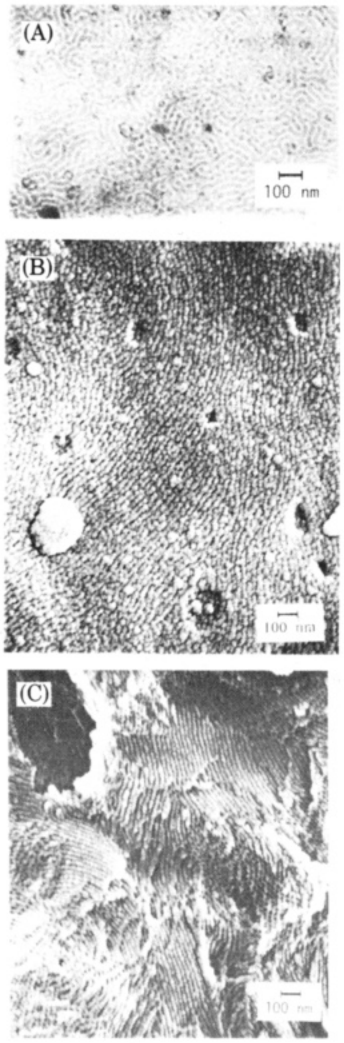

Figure 2. Electron micrographs of the thin film of block copolymer **2** cast from MIBK observed by TEM (A) and the surface (B) and the cross section (C) of the ozone-treated and rinsed film observed by SEM, the scale mark indicates 100 nm.

film, **2**, and the porous membrane were investigated by means of transmission and scanning electron microscopies, respectively. The lamellar structure of the segregated microphase was observed on the surface of the original film as shown in Figure 2A. After the film was rinsed and treated with ozone and methanol, a rugged surface of a similar lamellar pattern emerged (Figure 2B). The shadowed and ridged lines may correspond to the etched polyisoprene and remaining poly(**1**) domains, respectively. The scanning electron micrograph of a cross section of the treated film also exhibited lamellar morphology (Figure 2C), suggesting that the hollow domain continued through the film. The pore width seems to be 10 nm although the periodicity distance of the polyisoprene domain of the original film is about 20 nm, which is also reasonable value based on the polyisoprene block length. Such shrinkage of pores might be caused by leaching out the cleaved products and gold coating on the sample would also affect the electron microscopic observation.

The surface area of the porous membrane was measured by BET method to be 74 m^2/g. This large value indicates that the hollow domain is not a closed and/or shallow groove but rather is a continuous channel.

The results of IR and BET measurement, elemental and gravimetric analyses, and electron micrographic observation substantiated the formation of the microporous membrane, whose structure was similar to that of segregated microphase of the original block copolymer. A further work on the synthesis and detailed characterization of the membranes with different controlled pore sizes is now in progress.

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Registry No. (Isoprene)((4-vinylphenyl)dimethyl-2-propoxysilane) (block copolymer), 102394-54-7.

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(4) Assuming that isopropoxysilyl group was almost converted into siloxane linkage and that polyisoprene chains were completely cleaved and leached out, the weight of original film (**2**, 250 mg) should reduce to 120 mg, but the weight of produced porous film was actually 150 mg. The difference (30 mg), corresponding to about 30 wt % of polyisoprene block (88 mg) of the original film, may be attributable to residual polymer chain attached to the micropore by a covalent bond.
(5) The elemental composition is calculated on the following assumptions: all isopropoxysilyl groups are converted into siloxane linkages, 70 wt % of polyisoprene chain is decomposed, and the all C=C bonds of residual polyisoprene chains are oxidized.

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Ferrocenyl Containing Polysilanes[1]

Organopolysilanes, high molecular weight polymers containing only Si atoms in the backbone, $(R''R'Si)_n$, have attracted considerable recent interest due to their use as photoresists,[2-4] perceramic and ceramic doping materials,[5,6] dopable semiconductors,[6] and photoconducting[7] and nonlinear optical materials.[8] To date, the substituent groups R″ and R′ have been limited to organic radicals such as phenyl, alkyl, and trimethylsilyl groups.

We have been interested for a long time in the chemical and physical properties of transition-metal-substituted silanes, including oligosilane, and have found that the location of a transition-metal center in an oligosilane dramatically alters these properties. For example, oligosilanes are significantly more susceptible to photochemical deoligomerization when directly bonded to the iron atom in $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ systems, while migration from the iron atom to the cyclopentadienyl ligand removes this activation.[9,10]

Such dramatic changes in photochemical properties suggested to us that preparation of transition-metal-substituted high molecular weight polysilanes would produce a new class of these interesting polymers with many unique properties. In this initial report on our studies we present the first example of such compounds in which copolymerization of ferrocenylmethyldichlorosilane, $FcMeSiCl_2$, Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$, and phenylmethyldichlorosilane, $PhMeSiCl_2$, has been successfully accomplished.

Copolymerization was effected by the procedure of Wurtz-type coupling as outlined in reaction 1.[11]

$$FcMeSiCl_2 + nPhMeSiCl_2 \xrightarrow{\text{Na/solvent}} [(FcMeSi)(PhMeSi)_n]_m \quad (1)$$

Table I
Physical Properties of New Poly(ferrocenylsilanes)

PhMeSi/ FcMeSi					
react	prod	$M_w \times 10^{-3\,a}$	P^b	λ_{max}	T_g, J/g
5^c	6	12	*e*	339 450^g	96 (0.16), 131^f
5^d	6	80, 2.5	4.0	339, 450	
10^c	12	150, 2.5	0.3	340	130 (0.14)
10^d	12	390, 4.0	6.0	340	
25^d	27	200, 11.0	1.4	340	133 (0.42)

[a] Determined by SEC, using polystyrene standards. [b] Proportion of high to low molecular weight fractions.[a] [c] Reaction solvent, 80:20 toluene/heptane. [d] Reaction solvent, toluene. [e] Monomodal. [f] Very small. [g] This band, ascribable to the Fc units, has an $\epsilon \simeq 36$, which based upon the relative amount of Fc in the polymer translates into an $\epsilon \simeq 180$ for the individual Fc unit in accord with published data for FcR and $FcSiR_3$.[13,14] Values of ϵ are $\simeq$9–12 000 for the band at 340 nm for the various copolymers reported.

Under these conditions, solvent = toluene or toluene/heptane mixtures, n = 5, 10, 15, and 20, the reactions resulted in high molecular weight polymers, soluble in organic solvents. At the present time our attempts to make homopolymers $(FcSiMe)_n$ have not been successful. Stoichiometries of the various copolymers were determined by using ^1H NMR spectroscopy and clearly indicate that statistical incorporation of the monomers occurs for all the initial relative reactant compositions. The physical properties of the copolymers are presented in Table I. It may be seen that very high molecular weight materials are available, and in those examples where bimodal molecular weight distributions are obtained, the proportion of the high molecular weight component may be high.[12] At present we have made no effort to maximize yields or product MW distribution. The various T_g values are, as expected, similar to those of the homopolymer $(PhMeSi)_n$, but it is of interest that in the case of the 1:5 copolymer there are two reproducible thermal events. It is also noteworthy that, apart from a weak Fc transition between 450 and 500 nm, the lowest energy electronic excitation is at the same wavelength in the copolymers as in the homopolymer $(PhMeSi)_n$, 340 ± 1 nm.

Of initial interest were the photochemical properties of these new materials. The new polymers are photosensitive with respect to depolymerization, exhibiting both the characteristic decrease in optical density and blue shift upon exposure to irradiation. Figure 1 illustrates such photochemical depolymerization and the related data for the homopolymer $(PhMeSi)_n$ when irradiated under identical conditions of concentration, irradiation time, and flux in a side-by-side experiment. These data clearly indicate that incorporation of a ferrocenyl unit into the polymers provides a degree of photostabilization to the $(Si)_n$ backbone. Doping experiments in which varying amounts of FcH were added to $(PhMeSi)_n$ and $(n\text{-PrMeSi})_n$ to correspond to the amount of Fc incorporation in the homopolymers indicated no significant reduction in photodepolymerization of the polysilane.

Our studies on related metal incorporation into high molecular weight polysilanes is continuing, as are detailed studies on the electrical, photoconducting, and other properties of the ferrocenyl systems.

Experimental Section. In a typical reaction, a mixture of 0.6 g (2.0 mmol) of $FcSiMeCl_2$ and 2.0 g (10.5 mol) of $PhMeSiCl_2$ in 100 mL toluene heated to reflux in a foil-covered three-necked round-bottomed flask was treated dropwise with 1.6 g (27.5 mmol) of a 40% Na dispersion in light oil. The dark blue solution was refluxed for 2 h and cooled to room temperature. A few drops of MeOH was added to remove excess Na, followed by treatment with a saturated $NaHCO_3$ solution (20 mL) and 20 mL of toluene. Subsequent to separation and drying of the organic phase with $MgSO_4$, the solvent was removed under vacuum to yield an orange oil. Two precipitations from toluene with hexane and two from THF with methanol produced 80 mg of a cream-colored powder: ^1H NMR ($CDCl_3$) δ 6.9 (br d m, 5 H, aryl), 3.8 (br d m, 1.6 H, C_5H_n), –0.2, –0.5 (br d s, 3.6 H, SiMe); ^{13}C NMR ($CDCl_3$) δ 136.4, 135.0, 127.1 (br d s, aryl), 73.3, 68.0 (br d s, C_5H_n), –6.2 (br d s, SiMe).

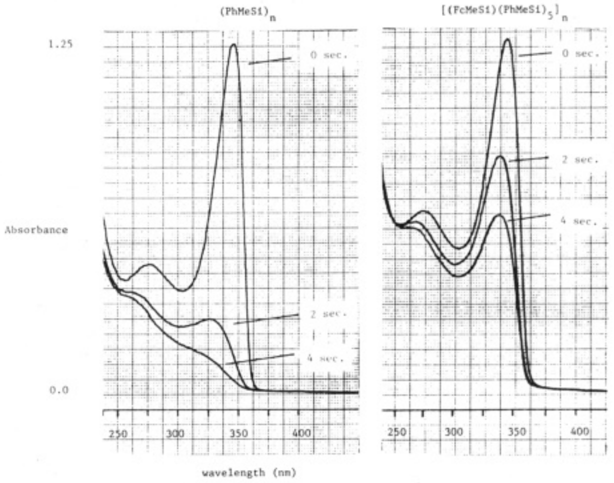

Figure 1. Photolysis of polysilane polymers in THF solution.

Photochemical experiments were conducted in a Rayonet-type RS photochemical reactor equipped with RUL-3000A lamps.

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Registry No. $(FcMeSiCl_2)(PhMeSiCl_2)$ (copolymer), 111689-16-8.

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Thermotropic Liquid Crystals of Polyesters Having a Mesogenic *p*,*p*′-Bibenzoate Unit. 1. Smectic Mesophase Properties of Polyesters Composed of *p*,*p*′-Bibenzoic Acid and Alkylene Glycols

In a previous paper,[1] Krigbaum and Watanabe reported a study of smectic A phase (S_A) of the homologous series of polyesters prepared by *p*,*p*′-bibenzoic acid and its tetra-, hexa-, octa-, and decamethylene glycols. These polymers are designated BB-*n*, where *n* is the number of methylene units in the diol. The BB-4 and BB-6 polymers form a thermotropic smectic phase which could be identified as S_A by mutual miscibility studies with a known low molecular weight mesogen, TBBA. The S_A structure is also supported by the X-ray observation that the smectic layer spacing is slightly shorter than the fully extended length of the repeating unit for both BB-4 and BB-6.

We here investigated the polymeric smectic mesophase by extending the study to the homologous series BB-4, BB-5, BB-6, BB-7, BB-8, and BB-9. Interestingly, all polymers invariably form the smectic phase and its isotropization temperature, T_i, and entropy, ΔS_i, exhibit an even–odd oscillation with the number of intervening methylene units, *n*, which has been generally observed for the nematic mesophases.[2-4] The even–odd nature of methylene units is also reflected in the thickness of the smectic layer. Some discussion will be made on a relation between the smectic mesophase properties and the even–odd nature of methylene units.

All the polymers used here were synthesized by melt transesterification from diethyl *p*,*p*′-bibenzoate and the appropriate diol with isopropyl titanate as catalyst. Inherent viscosities, as determined at 25 °C by using 0.50 g/dL solutions in a 60/40 w/w mixture of phenol and tetrachloroethane, ranged from 0.2 to 0.4 dL/g for all polymers.

In Figure 1, the representative DSC curves of polymers are shown for BB-4 and BB-5. Both indicate two peaks on heating and cooling; the peak at lower temperature (T_1) corresponds to the crystal to liquid crystal transition and the higher temperature (T_2) peak to the liquid crystal to isotropic transition. The mesophase on heating arises in a narrow temperature region and this trend becomes remarkable as *n* increases. Hence, there is a monotropic appearance of mesophase in BB-7, BB-8, and BB-9, in which the mesophase is observed only on cooling.

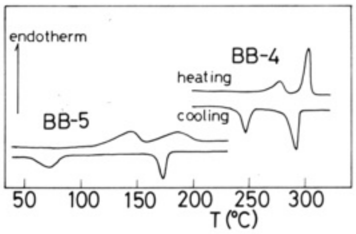

Figure 1. DSC thermograms of BB-4 and BB-5.

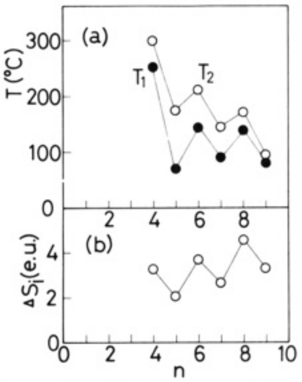

Figure 2. Variation of (a) transition temperatures (T_1 and T_2) and (b) transition entropy (ΔS_i) with the number (*n*) of methylene units.

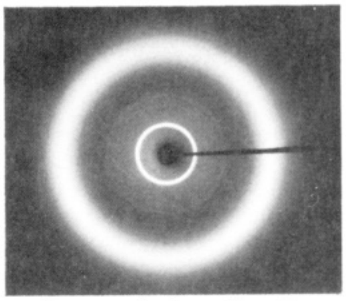

Figure 3. X-ray photograph of unoriented mesophase of BB-5 taken at 150 °C.

Data obtained from the cooling curves, concerning the temperature range of the mesophase and the enthalpy and entropy changes upon isotropization, are collected in Table I. In Figure 2a is shown the behavior of the two transition temperatures as a function of the number, *n*, of methylene units in the alkanediol. Both temperatures exhibit the usual even–odd oscillation, and the vertical spacing of the two points, which represents the temperature span of the mesophase, becomes narrow as *n* increases. Similarly, an even–odd oscillation is observed in the isotropization entropies, ΔS_i, as shown in Figure 2b, and for the isotropization enthalpies with higher values in the even-membered polymers (see the fourth and fifth columns in Table I). It seems unlikely that the entropies of the isotropic phases of the even and odd members would differ by this magnitude, leading to the conclusion that the mesophase of the even-membered series is more highly ordered.

In optical microscopic observation, the mesophases of even-membered polymers appear as batonnets on cooling from the isotropic melt and they coalesce to make a well-developed fan-shaped texture with focal-conic domains. Batonnets and the fan-shaped texture are characteristic of the layer structure of smectic mesophase. In the odd-membered mesophases, a similar fan-shaped texture is observed, although it is composed of the finer focal-conic domains than those in the even members.

X-ray diffraction clarifies the smectic mesophase in both series. Here, the diffraction pattern of the mesophase was recorded for the polymer held in a capillary which was cooled from the isotropic phase to the mesophase. The diffraction pattern, as representatively shown for BB-5 in Figure 3, consists of one or two sharp inner reflections and

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