TABLE I
ZERO SHEAR VISCOSITY FOR 30 AND 40% POLYSTYRENE SOLUTION AT 25°

M_w	M_w/M_n	Viscosity η_0, poise (40% soln)	Apparent shear rate, sec^{-1}	Viscosity η_0, poise (30% soln)	Apparent shear rate, sec^{-1}
1.80×10^{6}	1.20	3.16×10^{8}	2.21×10^{-6}	2.00×10^{7}	3.23×10^{-6}
		4.08×10^{8}	2.02×10^{-6}	1.70×10^{7}	5.00×10^{-6}
8.60×10^{5}	1.15	5.00×10^{7}	5.23×10^{-4}	2.20×10^{6}	5.41×10^{-5}
		5.02×10^{7}	5.33×10^{-4}	1.68×10^{6}	9.98×10^{-4}
		5.11×10^{7}	5.11×10^{-4}	1.91×10^{6}	7.82×10^{-5}
4.11×10^{5}	1.06	4.01×10^{6}	7.99×10^{-4}	1.91×10^{5}	1.60×10^{-4}
		3.98×10^{6}	8.23×10^{-4}	1.61×10^{5}	2.62×10^{-4}
1.60×10^{5}	1.06	1.46×10^{5}	1.41×10^{-3}	7.20×10^{3}	1.16×10^{-2}
		1.44×10^{5}	2.01×10^{-3}	7.00×10^{3}	2.02×10^{-2}
		1.40×10^{5}	2.74×10^{-3}		
9.70×10^{4}	1.06	3.90×10^{4}	4.44×10^{-3}	1.88×10^{3}	2.34×10^{-2}
		3.36×10^{4}	4.51×10^{-3}	2.04×10^{3}	1.71×10^{-2}
		3.32×10^{4}	4.54×10^{-3}	1.97×10^{3}	2.22×10^{-2}
5.10×10^{4}	1.06	1.02×10^{4}	8.45×10^{-3}	7.81×10^{2}	1.32×10^{-2}
		9.13×10^{4}	1.25×10^{-2}	6.98×10^{2}	7.03×10^{-1}
		9.81×10^{4}	7.81×10^{-3}	6.97×10^{2}	3.00×10^{-1}
2.04×10^{4}	1.06	2.57×10^{3}	2.01×10^{-3}	2.46×10^{2}	2.40×10^{-1}
		2.52×10^{3}	3.56×10^{-3}	2.91×10^{2}	1.80×10^{-1}
1.03×10^{4}	1.06	1.15×10^{3}	7.82×10^{-2}	1.50×10^{2}	3.58×10^{-1}
		1.13×10^{3}	8.21×10^{-2}	1.36×10^{2}	4.30×10^{-1}
2.10×10^{3}	1.10	2.17×10^{2}	2.31×10^{-2}	2.82×10^{1}	1.21×10^{-1}
		2.20×10^{2}	1.23×10^{-2}	2.46×10^{1}	2.02×10^{-1}

Kelly[21] and by Fox and Allen[22] all yield a slope of 1.0 at low molecular weights. It is also significant to note that the log–log plot of η_0 *vs.* M does not abruptly change in slope from 1.0 to 3.4 but that it changes gradually. The region over which this change in slope occurs was defined by Sell[23] as the region of partial entanglement and was discussed further by Wolkowicz[24] and Forsman.[25] We have, then, defined M_c by the intersection of the two straight-line sections of the curve.

Apparent abrupt changes in the slope of log–log plots of η_0 *vs.* M, as well as η_0 *vs.* C, have been used as a measure of the characteristic entanglement composition,[26] and several investigators have proposed various relationships between molecular weight and concentration that determine the inception of molecular entanglement. All these equations are essentially of the same form with various power dependencies on M_c. Onogi[27] derived an expression based on a packed spheres model which predicted that $(W\rho M_c^{0.5})$ should be a constant, where W is the weight fraction of the polymer in solution. He has also recently pointed out that[28] the characteristic constant defining entanglement composition can be derived from the theory of Bueche to be $(W\rho M_c^{0.83})$. Ferry and coworkers[20] reported it to be $(W\rho M_c^{0.68})$. There are, however, other results[5,19] indicating that $(W\rho M_c)$ is constant for data on some of the same systems for which other dependencies have been given.[26] Our experimental results on concentrated solutions of narrow distribution polystyrene in di-2-ethyl hexyl phthalate agree well with this last, and simplest, expression. We found $(W\rho M_c)$ to be equal to 3.00×10^4 and 3.03×10^4 for the 40 and 30% solutions (assuming constant density), which is in good agreement with (although slightly lower than) most values reported in the literature for both bulk polymer and solutions.[26]

Acknowledgment. This work was supported by the National Science Foundation through Grant Gp 3059.

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Production of Organometallic Polymers by the Interfacial Technique. IV. Synthesis of Poly(silylalkylenediamines) by the Interfacial Technique

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Aylett[1] has recently reviewed the subject of silicon–nitrogen polymers. He notes that by contrast to Si–O polymers, polymers with Si–N bonds in the main chain have received little attention mainly because of a lack of suitable preparative methods. The review includes a review of polymer types concerned within

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(1) B. J. Aylett, *Organometal. Chem. Rev.*, **3**, 151 (1968).

TABLE I

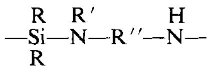
PHYSICAL PROPERTIES OF POLY(SILYLALKYLENEDIAMINES)[a]

	Diamine		
	Ethylendiamine	1,3-Propanediamine	Phenyldrazine
Per cent yield	86	84	73
Melting range, °C	165–172	187–196	62–70
LVN, ml/g	14	6	6
Color	White-light tan	White-light tan	Yellow-brown
Physical appearance	Powdery	Powdery	Glassy
Polymer soluble in	Acetonitrile,[b] dimethylformamide (DMF), dimethyl sulfoxide (DMSO),[b] dichloromethane,[b] acetone	Chloroform, DMF acetonitrile,[b] acetone	Heptane,[b] ether, carbon tetrachloride, DMSO, acetone
Polymer insoluble in	Carbon tetrachloride, ethyl ether, benzene, cyclohexane, water	Water, cyclohexane, ether, heptane	Water, cyclohexane

[a] 0.018 mol of diphenyldichlorosilane, 0.090 mol of diamine, 0.036 mol of sodium hydroxide, 50 ml of cyclohexane, 3 min stirring time. [b] Solubility less than 1 g/100 ml.

this paper. For an additional review of silicon–nitrogen polymers, see ref 2.

Carraher[3] recently reported the first interfacial synthesis of polyalkyloxysilanes. Synthesis was effected by condensing dichlorosilanes with diols in stirred and unstirred systems. The first interfacial synthesis of poly(silylalkylenediamines) of the below form is reported here.



$$-\overset{R}{\underset{R}{Si}}-\overset{R'}{N}-R''-\overset{H}{N}-$$

I

Experimental Section

Stirred and unstirred polymerization procedures as described by Carraher[3] were followed. Infrared spectra were obtained on a Beckman IR-10 using potassium bromide pellets. The spectra are in agreement with a repeating unit exemplied by I (where R'' is not present in the case where the diamine is phenylhydrazine). Viscometry was carried out in acetone at 30° using a Cannon-Ubbelohde 50 viscometer. Melting ranges were taken on a Fisher-Johns melting point apparatus at a heating rate of 2°/min and were taken to be the temperature at which melting initially began to where melting was complete. Melting ranges obtained are given without claim to being a measure of the glass transition temperature or the crystalline melting point.

Polymer gross hydrolytic stability tests were carried out as follows on the products from diphenyldichlorosilane and ethylenediamine. Polymer samples were ground to a fine powder and 0.5 g was placed in each of four separate flasks. Liquid, as described below, was added to each flask and the mixture periodically shaken for 2 days. The contents were placed in watch glasses and the liquid portion was evaporated off using a steam bath. Viscometry was conducted on the remaining residues. Samples 1 and 2 contained polymer with 80 ml of distilled water. Sample 1 was maintained at room temperature (about 25°) for the test period. The limiting viscosity number (LVN) of sample 1 decreased from 14 to 6 ml/g. Sample 2 was heated to 70–75° for the test period and its LVN decreased to 5 ml/g. Sample 3 was prepared by initially dissolving the polymer in 40 ml of acetone and then adding it to 40 ml of distilled water. The mixture was maintained at room temperature for the test period. (Upon addition of the acetone solution to water precipitation of the polymer occurred.) The LVN decreased to 6 ml/g. Sample 4 was prepared by initially dissolving the polymer in 79 ml of acetone and then adding to it 1 ml of distilled water (no precipitation occurred). The mixture was maintained at room temperature during the test period. The LVN decreased to 2 ml/g.

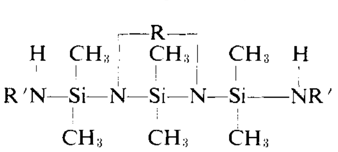
Results

Results for polymers produced by the stirred method (using a Waring Blendor (No. 7700-S) stirrer and a 1-pint Kimax milling jar as described by Carraher[3]) appear in Table I. Similar polymers also were produced using the unstirred interfacial technique as described by Carraher.[3] Diphenyldichlorosilane (0.018 mol) in 50 ml of cyclohexane was condensed with ethylenediamine (0.090 mol) in the presence of 0.036 mol of sodium hydroxide. The phases were allowed to sit together for 1 week. A 51% yield of polymer was produced. The product was light brown and waxy in appearance, with a melting range of 60–73°.

Discussion

Aylett[1] states that many of the obvious routes to polymers containing Si–N units result in cyclic oligomers rather than polymers. Several attempts have been made to inhibit the formation of cyclic products.

Breed, Elliot, and Ferris[4–6] have investigated systems employing sterically hindered monomers such as II. This approach has been largely successful but involves the use of monomers which are not readily available. Other approaches have generally been successful.[1]



$$R'\overset{H}{N}-\underset{CH_3}{\overset{CH_3}{Si}}\overbrace{-N-\underset{CH_3}{\overset{CH_3}{Si}}}^{R}-N-\underset{CH_3}{\overset{CH_3}{Si}}-\overset{H}{N}R'$$

Aylett[7] recently reported the formation of polymers containing Si–N bonds from the reaction of organodisilylamine in the presence of a base catalyst at −50

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(2) H. R. Allcock, "Heteroatom Ring Systems and Polymers," Academic Press, New York, N. Y., 1967.

(3) C. E. Carraher, *J. Polym. Sci.*, in press.

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(7) B. J. Aylett, British Patent 1,123,252 (1968).

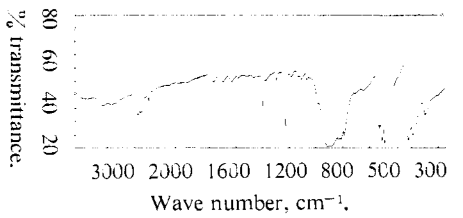


Figure 1. Infrared spectrum of poly[iminoethylenimino-(diphenylsilylene)].

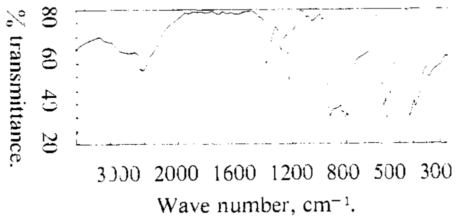
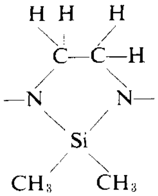


Figure 2. Infrared spectrum of poly[(phenylimino)imino-(diphenylsilylene)].

to 200° in an inert atmosphere. The products are not well defined as to linearity or molecular weight.

Kummer and Rochow[8] and others [9-12] have noted a strong tendency for the formation of five-membered cyclic rings as III from the condensation of diamines as ethylenediamine with dimethylsilicon containing mono-



III

mers. Furthermore the infrared spectra of these five-membered rings display a characteristic sharp absorption at 1340 cm^{-1}.[8,13] There are no peaks in the region of 1340 cm^{-1} in the spectra of the products reported in this paper (for instance Figures 1 and 2) indicating that five-membered rings of this type are absent. This is in agreement with the results reported by Minné[14] where he reports an essentially linear product from the reaction of diphenyldichlorosilane with ethylenediamine.

In addition the product of diphenyldichlorosilane and ethylenediamine reported in this paper is of intermediate molecular weight. Using the viscosity–number-average molecular weight relationship given by Barry[15] for polysiloxanes in toluene, a LVN of 0.14 dl/g corresponds to a number-average molecular weight of 21,000 and a number-average degree of polymerization of 88. Thus the interfacial method is capable of producing intermediate molecular weight poly(silylalkylenediamines).

The interfacial technique is, in general, a simpler, faster way of obtaining polymers with the Si–N type of bonding in the backbone than previously employed methods. It can be used in systems employing or producing temperature-sensitive compounds, since the reaction can be conducted at or below room temperature. It also employs comers which are commercially available. It is noted that the procedure reported in this paper is limited to use of primary or secondary diamines which are liquid at or near room temperature.

It was found that when the diamine was 1,3-propanediamine or phenylhydrazine, smaller chains were formed. (We are continuing to investigate the interfacial synthesis of polysilazanes by the modified interfacial technique of Carraher[3] as well as the further characterization of the products.) The difference in molecular weight of the products is clearly evident in their solubility behavior. The intermediate molecular weight products in which the diamine was ethylenediamine are generally soluble only in dipolar aprotic solvents, whereas the low molecular weight products in which the diamine was 1,3-propanediamine or phenylhydrazine are soluble in many other organic solvents (Table I). The latter observation is in general agreement with the solubility properties reported for other poly(silylalkylenediamine) products (see, for instance, ref 4, 8, 16, and 17).

Poly(silylalkylenediamines) generally have poor hydrolytic stability. The tests performed in this study give admittedly only approximate information concerning the stability of the polymers. It can be argued correctly that one reason for the relatively good hydrolytic stability exhibited by the products is that they are hydrophobic and that "wetting" does not occur to any large degree. Even in the case where polymer was initially dissolved in acetone and subsequently added to water, the polymer precipitated on addition to water possibly resulting in only a small degree of "wetting." In the test where polymer was initially dissolved in acetone and then only a small amount of water added, so as not to produce precipitation, the LVN dropped more markedly than in the other tests presumably due to a greater degree of polymer "wetting," and consequently degradation, in solution. Further work is being done in this area.

Acknowledgment. This research was supported in part by an American Chemical Society Petroleum Research Grant No. 1338-G13.

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