The Synthesis and Gas-Transport Properties of Some Hydrosilylation Condensation Polymers

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SYNOPSIS

High-permeance collection layers are needed in composite membranes but few polymers have the required permeability. Hydrosilylation condensation polymers, because of their high silicon content, were thought to be good candidates to have high permeabilities. Several novel polymers were made and a new and simpler synthesis of ethynylated silanes is reported. One polymer, poly(divinyldimethylsilane-co-1,4-bis[dimethylsilyl]benzene), appears to be of a liquid crystalline nature and has a low oxygen permeability (1.10 barrers). Two others [poly(diethynyldimethylsilane-co-1,4-bis[dimethylsilyl]benzene and poly(divinyldimethylsilane-co-p,p'diethynylbiphenyl-co-tetramethyldisiloxane)] were viscous liquids that could be thermally cured to give elastomers with oxygen permeabilities of ~ 85 barrers. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

High-permeability polymers are of interest to serve as collection layers in composite membranes.[1,2] In this application, the collection layer is located between the discriminating layer and the porous support and facilitates the transport of the gas to a pore (Fig. 1).

The ideal collection layer should have a permeance an order or more of magnitude higher than the selective layer so that the transport properties are determined by the selective layer and can be easily applied, preferably from solution as a coating to the support. The collection layer should not interfere with the formation of the selective layer that might also be deposited as a coating from solution.

Organosilicon polymers have the highest gas permeabilities, i.e., polytrimethylvinylsilane, 50 barrers[3]; polydimethylsiloxane, 540 barrers; and polytrimethylsilylpropyne, 3000 barrers.[4] The inclusion of silicon into a polymer generally lowers the polymer solubility parameter and therefore increases the gas solubility, and also, due to the larger size of silicon, the polymer packing may be disrupted, increasing the gas diffusivity. Increasing either the solubility or diffusivity will increase the permeability, which is the product of solubility and diffusivity.

Condensation polymers made by the hydrosilylation of difunctional terminal ethene or ethyne groups with dihydrosilanes are candidates for collection layers due to their high silicon content. This report deals with the synthesis, characterization, and gas-transport properties of several novel hydrosilylation condensation polymers.

EXPERIMENTAL

Materials

All solvents were obtained from commercial sources. The silane monomers (Huls) were distilled before use. The diethynylbiphenyl was obtained from J. Brewbaker of the Dow Chemical Co. The sodium acetylide, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo(8.8.8)-hexacosane (Kryptofix™ 222) and hexachloroplatinoic acid (Aldrich) were used as received.

Equipment

The ^{1}H and ^{13}C-NMR spectra were obtained using a Varian Gemini 300 spectrometer. Size exclusion chromatography (SEC) was done with tetrahydrofuran eluant on a Waters Model 150°C instrument containing Toyo Soda columns packed with TSK-gel. Monomer concentrations were determined by
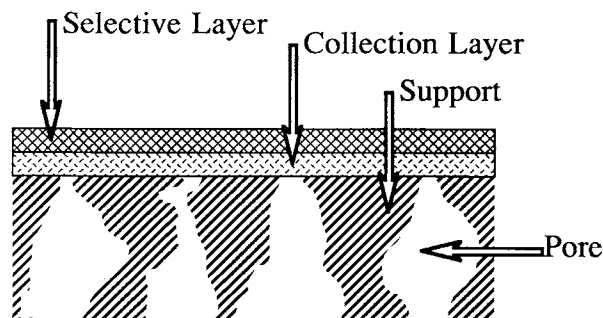
Figure 1 The microstructure of a composite membrane.

gas–liquid chromatography. The DSC thermograms were obtained with a DuPont 912 differential scanning calorimeter.

Diethynyldimethylsilane Synthesis

A sodium acetylide (1.64 g, 34.1 mmol, dispersed in 10.0 mL of light mineral oil/xylene) slurry was allowed to settle, and the light mineral oil/xylene was removed and replaced with toluene ($\sim$ 25 mL). The liquid phase was removed and replaced four more times before Kryptofix™ 222 (0.050 g, 0.13 mmol) was added. Dimethyldichlorosilane (2.0 mL, 16.2 mmol) was then added dropwise to the stirred reaction mixture such that the temperature did not exceed 30°C. The reaction was then allowed to proceed 72 h at 25°C. The mixture was filtered and analyzed by NMR techniques, giving a diethynyldimethylsilane yield of 1.1 g (63%).

Poly(divinyldimethylsilane-co-1,4-bis[dimethylsilyl]benzene) Synthesis

Divinyldimethylsilane (2.57 g, 22.9 mmol), 1,4-bis(dimethylsilyl)benzene (4.54 g, 23.3 mmol), and trivinylmethylsilane (60 μL, 0.371 mmol) were added to toluene (10 mL) at 24°C. Hexachloroplatinoic acid (20 μL of a 0.1 M 2-propanol solution) was then added to catalyze the polymerization. The temperature quickly rose to 75°C due to the reaction exotherm and was then raised to 102°C for 6 h. The mixture was then cooled to 24°C for 3 days before adding it to 300 mL of methanol to precipitate the polymer. The polymer was collected, washed, and dried, giving a gray solid (6.98 g, 98% yield) having an M_w = 113,000 based on polystyrene SEC standards. In a like manner, poly(divinyldimethylsilane-co - 1,4 - bis[dimethylsilyl]benzene - co - tetrame - thyldisiloxane) terpolymers were made by replacing some of the 1,4-bis(dimethylsilyl)benzene with tetramethyldisiloxane.

Poly(divinyldimethylsilane-co-p,p'-diethynylbiphenyl-co-tetramethyl disiloxane) Synthesis

Divinyldimethylsilane (2.50 mL,16.5 mmol), p,p'-diethynylbiphenyl (1.43 g, 7.08 mmol), tetramethyldisiloxane (4.20 mL, 23.7 mmol), trivinylmethylsilane (30 μL, 0.185 mmol), and polyhydromethylsiloxane (15 μL, 0.251 meq) were added to toluene (10 mL) and initiated with hexachloroplatinoic acid (20 μL of a 0.1M 2-propanol solution). The reaction exotherm peaked at 108°C before cooling to 75°C, where the reaction temperature was maintained for 6 h. The resulting polymer was a viscous liquid and was used without further purification.

Poly(diethynyldimethylsilane-co-1,4-bis[dimethylsilyl]benzene) Synthesis

A solution of diethynyldimethylsilane and oligomers in pentane (1.0 g, 2.90 meq acetylenic hydrogens), 1,4 bis(dimethylsilyl)benzene (670 μL, 3.00 mmol), and trivinylmethylsilane (60 μL, 0.370 mmol) were added to toluene (1.0 mL) and the polymerization catalyzed with hexachloroplatinoic acid (40 μL of a 0.1M 2-propanol solution). The reaction was run at 24°C and the mixture became very viscous and was used without further purification.

Poly(diethynyldimethylsilane-co-1,4-bis[dimethylsilyl]benzene) Synthesis

p,p'-Diethynylbiphenyl (1.00 g, 4.91 mmol), 1,4 bis(dimethylsilyl)benzene (1.18 mL, 5.28 mmol), and trivinylmethylsilane (60 μL, 0.37 mmol) were added to toluene (30 mL) and the polymerization catalyzed with hexachloroplatinoic acid (40 μL of a 0.1M 2-propanol solution). The reaction was run at 95°C for 2 h, allowed to cool to 24°C overnight, and heated a further 2 h at 95°C. The mixture was filtered and poured into methanol. The precipitated polymer was collected, washed, and dried 16 h at 45°C in a vacuum oven, giving a yellow solid (1.70 g, 98% yield) having an M_w = 175,000 based on polystyrene SEC standards.

Membrane Preparation

Membranes were made by several routes: homogeneous film casting and compression molding. For cast films the polymer was first dissolved in 10°25 mL of solvent at a concentration of 2–7% by weight, filtered through a 5 μ filter, and cast on a level glass
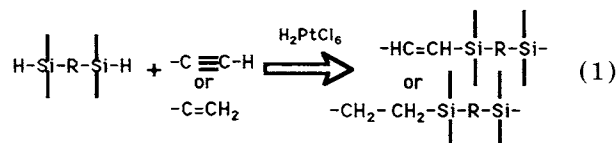
plate in a nitrogen dry box. After drying, the films were removed from the glass plate by immersing the plate in water and allowing the film to lift and float to the surface, giving a membrane $\sim$ 1–2 mil in thickness. Polymers that were compression-molded at $\sim$ 150°C gave membranes that were 75–125 μm thick.

Gas-transport Measurements

Gas permeabilities were measured at 30°C on a constant volume apparatus.[5] The diffusivities were determined by the time-lag method and solubilities calculated as the quotient of permeability and diffusivity.

RESULTS AND DISCUSSION

The hydrosilylation of terminal ethenes and ethynes is well known,[6] and there are a few examples of using this reaction to make condensation polymers.[7-9] During the condensation, [eq. (1)], chain extension occurs when a dihydrosilane adds anti-Markovnikov to a diethene or diethynyl-containing molecule:

$$H-\overset{|}{\underset{|}{Si}}-R-\overset{|}{\underset{|}{Si}}-H \; + \; \overset{-C \equiv C-H}{\underset{-C=CH_2}{or}} \; \overset{H_2PtCl_6}{\Longrightarrow} \; \overset{-HC=CH-\overset{|}{\underset{|}{Si}}-R-\overset{|}{\underset{|}{Si}}-}{\underset{-CH_2-CH_2-\overset{|}{\underset{|}{Si}}-R-\overset{|}{\underset{|}{Si}}-}{or}} \qquad (1)$$

In this type of polymerization, the highest molecular weights and, hence, the toughest polymers are obtained when the reactants are present in a 1 : 1 stoichiometry and the reaction proceeds to high conversions. In practice, an exact 1 : 1 stoichiometry and high conversions are difficult to achieve, so a small amount of a trifunctional monomer is often added to the reaction mixture to ensure that a high molecular weight polymer is produced. This phenomenon is illustrated in Table I, which shows the

Table I The Effect of Trivinylmethylsilane upon Poly(divinyldimethylsilane-*co*-1,4-bis[dimethylsilyl]benzene) Molecular Weight

Sample #	Mol Fraction Trivinylmethylsilane	Molecular Weight[a]
764-13-1	0.0000	29,000
764-24-1	0.0053	68,000
764-26-1	0.0080	113,000
764-27-1	0.0106	43,000

[a] SEC weight-average molecular weight based on polystyrene standards.
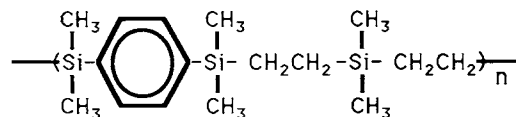

Figure 2 Poly(divinyldimethylsilane-*co*-1,4-bis[dimethylsilyl]benzene).

effect of trivinylmethylsilane concentration upon poly(divinyldimethylsilane-*co*-1,4-bis[dimethylsilyl]benzene) molecular weight.

At low molecular weights, < 100,000, the polymer is too brittle for its gas-transport properties to be evaluated, but by adding small amounts of a trifunctional monomer, the molecular weight is increased and the polymer is tough enough to be tested. At higher concentrations, the stoichiometry is altered enough so that the molecular weight decreases.Poly(divinyldimethylsilane-*co*-1,4-bis [dimethylsilyl]benzene) (Fig. 2) has some interesting and unexpected properties.

The polymer is soluble at room temperature but is crystalline as evidenced by DSC and X-ray diffraction data. The DSC thermogram (Fig. 3) shows in the first scan a broad endotherm with a peak at 138°C, while the second scan shows that the original peak is resolved into two endotherms centered at 123 and 137°C, respectively, perhaps indicating the presence of more than one crystalline phase. The X-ray diffraction pattern for the as-isolated polymer (Fig. 4) shows six major peaks with Bragg spacings of 6.21, 5.95, 5.68, 5.55, 4.80, and 3.38 Å. After melting and cooling, the 5.95 Å peak intensifies tremendously. This phenomenon is often seen with liquid crystalline materials when molecules become anisotropically ordered in the melt. This and the fact that the polymer is soluble below its melting point suggests that the poly(divinyldimethylsilane-*co*-1,4-bis[dimethylsilyl]benzene) has a low order of crystallinity typical of liquid crystalline polymers. When solutions of poly(divinyldimethylsilane-*co*-1,4-bis[dimethylsilyl]benzene) were cast, the polymer would phase-separate as it dried, preventing formation of a coherent film. However, films suitable for testing were easily made by compression molding. Some gas-transport properties are shown in Table II. The diffusivity decreases as the diameter of the permeating gas increases and the solubility decreases as the solubility parameter of the permeating gas decreases. The permeabilities are lower than expected, perhaps due to the crystalline nature of the polymer. To reduce the crystallinity, several terpolymers were made containing 0.125 and 0.250 mol fraction tetramethyldisiloxane (Fig. 5). This strat-
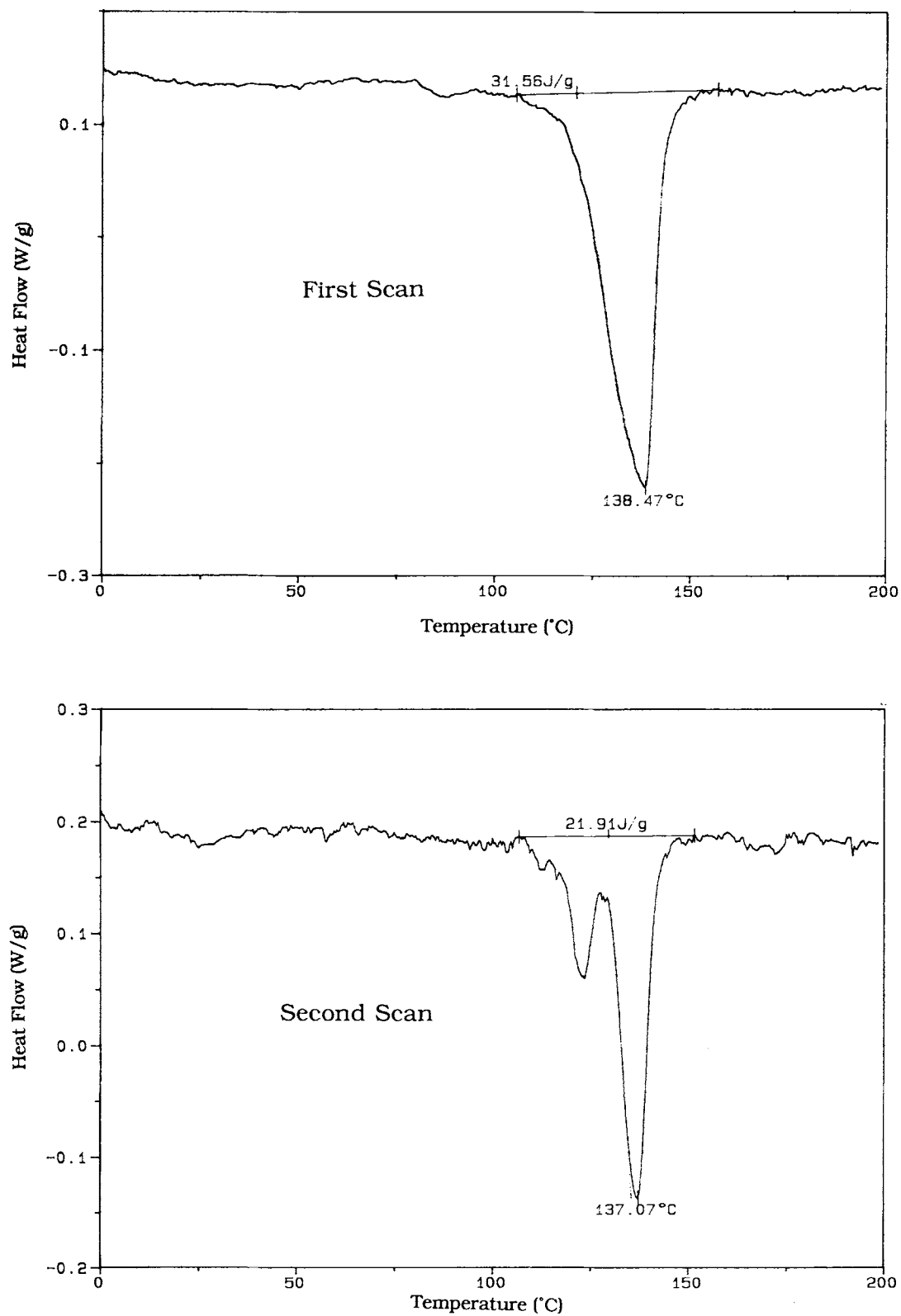
Figure 3 The DSC thermogram of poly(divinyldimethylsilane-*co*-1,4-bis[dimethylsilyl]benzene), first and second scan. The heating rate was 10°C/min to 200°C.
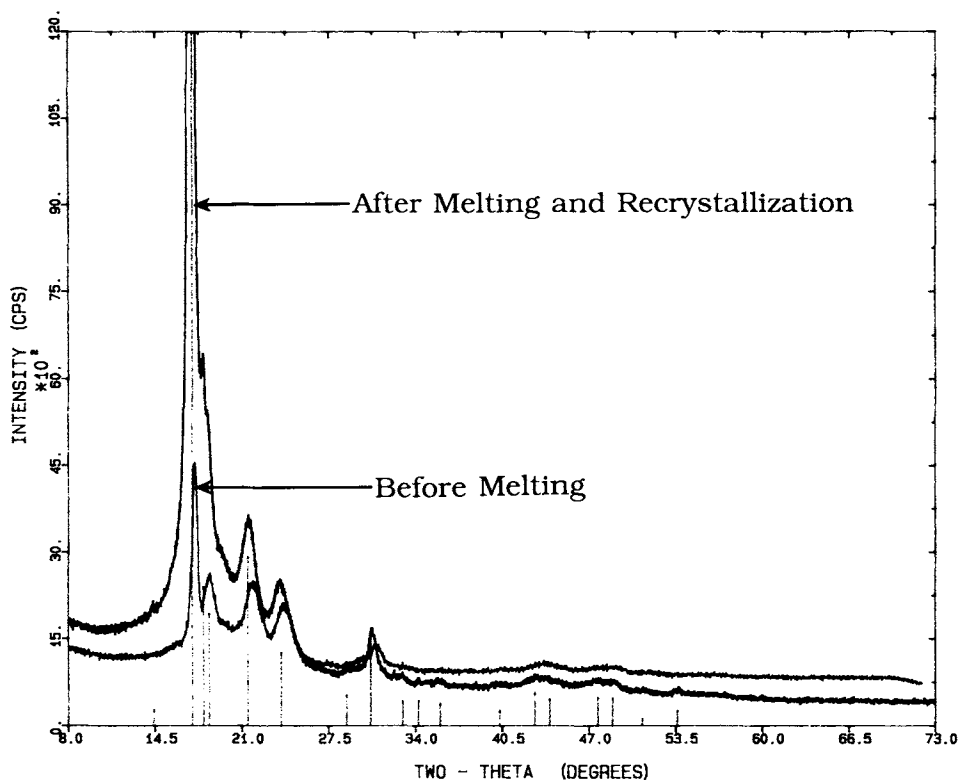
Figure 4 The X-ray diffraction pattern of poly(divinyldimethylsilane-co-1,4-bis-[dimethylsilyl]benzene) before and after melting and recrystallization.

egy worked, as evidenced by the DSC thermograms (Fig. 6), which show smaller melting endotherms (19.6 and 1.25 J/g, respectively) at lower melting temperatures (110 and 75°C, respectively). As a re-

sult of the lower polymer crystallinity and melting points, the polymers are tacky materials. The terpolymers have low molecular weights, 28,000 for the 0.250 tetramethyldisiloxane mol fraction terpolymer

Table II. Gas Permeability of Poly(divinyldimethylsilane-co-1,4-bis[dimethylsilyl]benzene) at 30°C

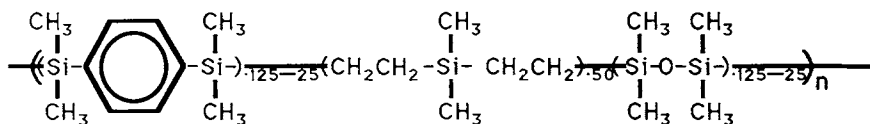| Gas	Permeability (barrers)	Diffusivity (cm^2/s)	Solubility (cm^3/cm^3 cmHg)
Helium	10.6	1.03×10^{-5}	1.03×10^{-4}
Oxygen	1.11	1.14×10^{-7}	9.74×10^{-4}
Nitrogen	0.257	4.60×10^{-8}	5.59×10^{-4}
Methane	0.530	2.30×10^{-8}	2.30×10^{-3}
Carbon dioxide	4.01	5.92×10^{-8}	6.77×10^{-3}

Figure 5 Poly(divinyldimethylsilane-co-1,4-bis[dimethylsilyl]benzene-co-tetramethyldisiloxane) terpolymer structure.
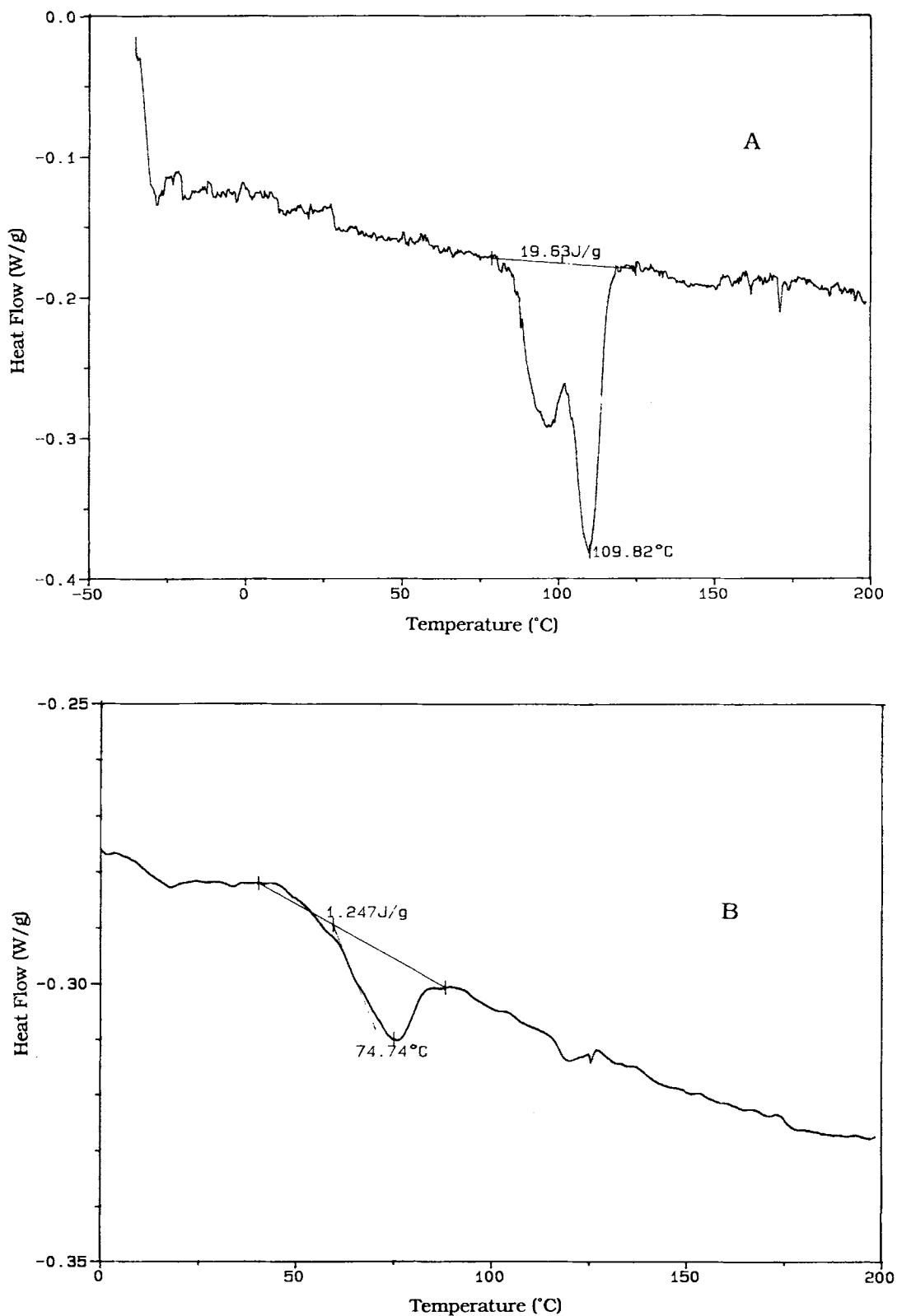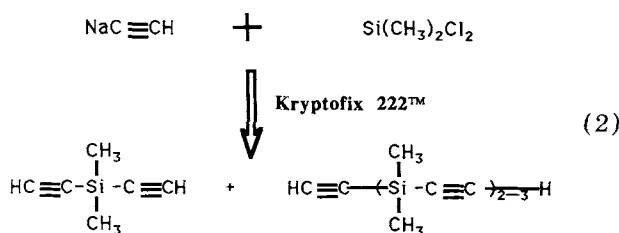
Figure 6   The DSC thermograms of poly(divinyldimethylsilane-*co*-1,4-bis[dimethyl-silyl]benzene-*co*-tetramethyldisiloxane), second scans: (A) the terpolymer with 0.125 mol fraction teramethyldisiloxane; (B) the terpolymer with 0.250 mol fraction teramethyldi-siloxane. The heating rate was 10°C/min to 200°C.

and 49,000 for the 0.125 tetramethyldisiloxane mol fraction terpolymer, so the films were not strong enough for gas-transport measurements.

Diethynyldimethylsilane is usually made by a Grignard route,[10] but a much simpler synthesis was used involving sodium acetylide. When dichlorodimethylsilane and sodium acetylide are mixed with solvent and heated, no reaction occurs, presumably because of the insolubility of sodium acetylide. However, upon the addition of small amounts of the kryptand, Kryptofix 222 (Fig. 7), the reaction proceeds rapidly.

It is believed the Kryptofix 222 complexes with and solubilizes a small amount of sodium acetylide that reacts quickly with the dichlorodimethylsilane and shifts the solubility equilibrium, drawing more sodium acetylide into solution until the reaction [eq. (2)] is complete:

$$NaC \equiv CH \quad + \quad Si(CH_3)_2Cl_2$$

$$\Downarrow \text{Kryptofix 222}^{TM}$$

$$HC \equiv C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-C \equiv CH \quad + \quad HC \equiv C-(\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-C \equiv C)_{2-3}H \quad (2)$$

The diethynyldimethylsilane can also react with dichlorodimethylsilane in the presence of sodium acetylide to form oligomers, which are the main coproducts. The mixture of monomer and oligomers was copolymerized with 1,4-bis(dimethylsilyl)benzene, giving a viscous liquid. Films of poly(diethynyldimethylsilane-co-1,4-bis [dimethylsilyl]benzene) cross-linked after heating at 125°C for 16 h to give an orange-colored rubber. An orange rubber film also resulted when poly(divinyldimethylsilane - co - p,p' - diethynylbiphenyl-co-tetramethyldisiloxane) was cured in a similar manner. This could be a desirable property for composite membrane applications as it would
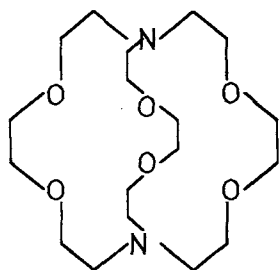

Figure 7 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8.]-hexacosane, Kryptofix™ 222.

Table III. Permeabilities of Poly(diethynyldimethylsilane-co-1,4-bis(dimethylsilyl)benzene) (I) and Poly(divinyldimethylsilane-co-p,p'-diethynylbiphenyl-co-tetramethyldisiloxane) (II) at 30°C

Sample	Permeability (barrers)		
	Oxygen	Nitrogen	Selectivity
I	85.0	33.0	2.6
II	84.1	33.1	2.5

render the polymer insoluble so that a selective layer could be coated on top of it without dissolving it away. The nitrogen and oxygen permeabilities of these polymers are given in Table III. The permeabilities, $\sim$ 85 barrers, are higher than most polymers but considerably lower than those of poly(dimethylsiloxane) and poly(trimethylsilylpropyne), making these hydrosilylation condensation polymers poor choices for collection-layer polymers.

Poly(p,p' - diethynylbiphenyl - co - 1,4 - bis [dimethylsilyl]benzene) (Fig. 8) could be made to a fairly high molecular weight, but films were too brittle for measuring gas-transport properties.

CONCLUSION AND SUMMARY

Several novel hydrosilylation condensation polymers were prepared and evaluated as high-permeability collection layers for composite membranes. A new and simple synthesis of ethynylsilanes, used as monomers, is reported. One of the polymers, poly(divinyldimethylsilane-co-1,4-bis[dimethylsilyl]benzene), is crystalline and could be molded to give tough films. The crystallinity appears to be mainly two-dimensional and of a liquid crystalline nature. Because of the high degree of crystallinity present, the permeability is too low to be used in collection layers. The degree of crystallinity can be reduced by incorporating a third monomer,
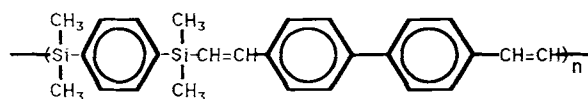

Figure 8 Poly(p,p'-diethynylbiphenyl-co-1,4-bis[dimethylsilyl]benzene).

tetramethyldisiloxane; unfortunately, the molecular weight is reduced to a level such that films suitable for gas-transport measurements cannot be prepared. Poly(p,p'-diethynylbiphenyl-co-1,4-bis[dimethylsilyl] benzene) also lacks sufficient strength for evaluation. Several other polymers, poly(diethynyldimethylsilane-co-1,4-bis[dimethl-silyl]benzene) and poly(divinyldimethylsilane-co-p,p'-diethynyl-biphenyl-co-tetramethyldisiloxane), are viscous liquids that can be thermally cured, a processing advantage, to give rubbery films. However, the permeabilities of these films, although high, are much lower than either polydimethylsiloxane or polytrimethylsilylpropyne.

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