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Synthesis and characterization of new pyrrole-containing polysilanes

P. Hegyes, J.-F. Dispa and L. Hevesi*
Department of Chemistry, Facultés Universitaires N.-D. de la Paix, 61 rue de Bruxelles, B-5000 Namur, Belgium

and L. Jeanmart, A.-F. de Mahieu, B. Jambe and J. Devaux*
Laboratoire de Physique et de Chimie des Hauts Polymères, Université Catholique de Louvain, 1 Croix du Sud, B-1348 Louvain-la-Neuve, Belgium

The syntheses of 'mixed' polysilanes of molecular weights $1400 \le M_w \le 8000$ composed of *N*-methyl-2,5-pyrrolylene, dimethylsilylene and tetramethyldisilylene units are described. Poly[(dimethylsilylen)-*N*-methyl-2,5-pyrrolylene] **3** was prepared from *N*-methyl-2,5-dibromopyrrole and dimethyldichlorosilane, and poly[(tetramethyldisilylen)-*N*-methyl-2,5-pyrrolylene] **5** was obtained by Wurtz polymerization of *N*-methyl-2,5-bis(dimethylchlorosilyl)pyrrole **4**. The 'mixed' polysilanes were characterized by size exclusion chromatography and by ^{1}H and ^{29}Si nuclear magnetic resonance and infra-red spectroscopies. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polysilanes; pyrrolylene; synthesis)

INTRODUCTION

Considerable interest and research efforts have been devoted world-wide over the last 15 years to silicon-based polymers possessing physical and chemical properties suitable for various technological applications[1,2]. As opposed to the all-silicon backbone polymers, polysilanes incorporating different carbon and/or heteroatomic units into their main chain have emerged recently. These units include acetylenic[3–9], aromatic[10–12], heteroaromatic[10,13,14], as well as ferrocenyl[15–17] moieties, which have been found to modify favourably the intrinsic physical properties of the polymers. For example, very high electrical conductivities have been obtained upon doping with Lewis acids for poly(disilylene)ethynylenes[3] and for terthiophene-containing polymers[13,14].

Herein we wish to report on new members of this type of 'mixed' polysilanes: one consisting of regularly alternating *N*-methyl-2,5-pyrrolylene and dimethylsilylene units, and one containing the same heteroaromatic fragment alternating with tetramethyldisilylene moieties.

EXPERIMENTAL

N-Methylpyrrole was distilled and stored over potassium hydroxide pellets; *N*-bromosuccinimide was recrystallized from hot water and dried before use; chlorosilanes were distilled from and stored over calcium hydride; and the reaction solvents (hexane, tetrahydrofuran (THF) and diethylether) were freshly distilled from sodium or from sodium benzophenone ketyl. All reagents were purchased from Sigma-Aldrich-Fluka (Bornem, Belgium) or from Acros Chimica (formerly Janssen Chimica, Geel, Belgium).

Gas chromatographic (g.c.) analyses of monomers were performed on a Hewlett–Packard 5890A gas chromatograph (SE-30 capillary column). G.c. mass spectrometry (m.s.) of monomer **4** was performed using a Hewlett–Packard 5890 Series II gas chromatograph fitted with a split–splitless injector and an HP7673A autosampler. The m.s. detector was an HP MSD 5971 Series.

^{1}H nuclear magnetic resonance (n.m.r.) spectra were recorded on a Jeol EX90 spectrometer. ^{29}Si n.m.r. spectra were recorded on a Bruker 500 MHz spectrometer using $CDCl_3$ as solvent and $Cr(acac)_3$ as relaxing agent. Tetramethylsilane (TMS) was used as internal standard.

The infra-red (i.r.) spectrum of polymer **5** was obtained on a Perkin–Elmer 1760 X FTIR spectrometer using KBr pellets. Ultraviolet (u.v.) spectra were recorded on a Philips PU 8720 UV/Vis spectrometer using CH_2Cl_2 solutions.

Gel permeation chromatography (g.p.c.) analyses were performed on a Waters instrument using five Ultrastyragel columns (10^6, 10^5, 10^4, 10^3 and 500 Å), a Waters 590 pump, a Waters 484 u.v. detector (254 nm) and unstabilized THF as solvent. Molecular weights are obtained using a polystyrene (PS) calibration.

Synthesis of N*-methyl-2,5-dibromopyrrole 1*

To a well-stirred solution of *N*-methylpyrrole (2.03 g, 25 mmol) in 40 ml of dry THF under argon and cooled to

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* To whom correspondence should be addressed

−78°C, *N*-bromosuccinimide (8.9 g, 50 mmol) was added in small portions (under argon stream) over a period of 2 h followed by another 1.5 h of stirring. The reaction could be monitored by gas chromatography: if traces of the monobromination product were detected in the reaction mixture at the end of the above reaction time, a slight excess of *N*-bromosuccinimide (2–5%) was added and the reaction continued for 1 h. Tributylamine (0.3 g) and solid sodium sulfite (0.5 g) were added, and the mixture allowed to warm to room temperature. Succinimide was precipitated with 150 ml of dry hexane and filtered. The organic solution was dried over magnesium sulfate and concentrated to give 6.44 g (including tributylamine) of essentially pure **1** as colourless crystals; these were immediately used without further purification (tributylamine does not interfere with subsequent synthesis steps).

^{1}H n.m.r. (CCl_4, ppm/TMS) of **1**: 3.55 (s, 3H, N–C$\underline{H}_3$); 6.05 (s, 2H, pyrrole β-$\underline{H}$).

Synthesis of polymer 3

To a solution of *N*-methyl-2,5-dibromopyrrole **1** (1.54 g, 6.4 mmol) in 25 ml of dry hexane, 8.45 ml (13.5 mmol) of n-butyllithium was added dropwise at room temperature under argon, and allowed to react for 5 h. To the white slurry so formed, 850 mg (6.4 mmol) of Me_2SiCl_2 dissolved in 10 ml of hexane was added slowly (2.5 h) by means of a pump-syringe. The mixture was stirred for 1 h longer at room temperature, then refluxed for 14 h. Methyllithium (0.4 ml, 0.64 mmol) was added and reacted for 1 h. The reaction mixture was diluted with toluene (25 ml), washed with water, saturated sodium chloride, dried over magnesium sulfate, and concentrated to give 980 mg of viscous brown oil which solidified on standing. The solid was dissolved in 3 ml of THF and the resulting solution added dropwise to 30 ml of methanol. The precipitate formed was filtered and dried to give polymer **3** as a light beige solid (97 mg, 11% yield).

Synthesis of N*-methyl-2,5-bis(dimethylchlorosilyl)pyrrole 4*

Dibromopyrrole **1** (prepared from 6.84 g, 84 mmol of *N*-methylpyrrole) was dissolved in 150 ml of dry ether and cooled to −78°C under argon. After dropwise addition of n-butyllithium (117 ml, 180 mmol, 1.54 M in hexane), the mixture was allowed to warm to room temperature for 1 h to give a light beige slurry of dilithiopyrrole **2**, which was slowly (1 h) transferred by a canula into a second double-necked round-bottomed flask containing 65 g (504 mmol) of dimethyldichlorosilane in 150 ml of ether maintained at 0°C under argon and magnetic stirring. The mixture was kept in the refrigerator overnight, filtered under argon, and the brown solution fractionated. Fractions collected between 80 and 90°C (0.4 torr) were redistilled to give 8.9 g (40%) of **4** as a colourless liquid (b.p. 78–80°C at 0.3 torr) that rapidly crystallized into long needles.

^{1}H n.m.r. ($CDCl_3$, reference CH_2Cl_2, ppm/TMS): 0.79 (s, 12H, SiC$\underline{H}_3$); 4.05 (s, 3H, N–C$\underline{H}_3$); 6.57 (s, 2H, pyrrole β-$\underline{H}$). ^{13}C n.m.r. ($CDCl_3$, ppm/TMS): 2.7 (Si$\underline{C}H_3$); 37.4 (N–$\underline{C}H_3$); 120.1 (pyrrole β-$\underline{C}$); 135.5 (pyrrole α-$\underline{C}$). ^{29}Si n.m.r. ($CDCl_3$, ppm/TMS): 9.3.

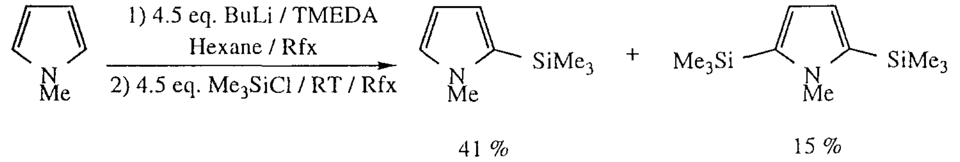
Synthesis of polymer 5

A 100 ml three-necked, round-bottomed brown flask, fitted with a condenser and an argon inlet, was first flame dried. Then, 50 ml toluene and 0.92 g sodium chunks (20% stoichiometric excess on **4**) were heated to gentle flux. *N*-Methyl-2,5-bis(dimethylchlorosilyl)pyrrole **4** (8.9 g) was then added dropwise through a capillary. The reaction was stirred for 4 h and then cooled to room temperature before adding 10 ml methanol. The organic phase was washed several times by water and decanted. The raw polymer was recovered by precipitation in methanol and dried at 60°C under vacuum. Due to the methanol addition the polymer chains are assumed to be methoxy-ended. Synthesis and work-up of the polymer were always undertaken either in brown glassware or under sodium yellow light, in order to prevent any possible u.v. degradation. Polymer yields of 40 to 60% were obtainable.

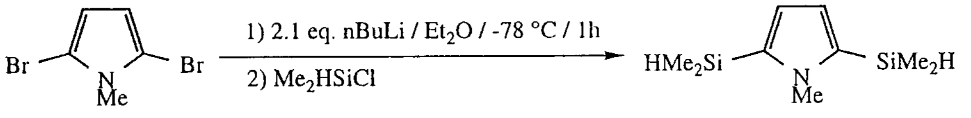
^{1}H n.m.r. ($CDCl_3$, reference CH_2Cl_2, ppm/TMS): 0.30 (s, 12H, SiC$\underline{H}_3$); 3.38 (s, 3H, N–C$\underline{H}_3$); 6.25 (s, 2H, pyrrole β-$\underline{H}$). ^{29}Si n.m.r. ($CDCl_3$, ppm/TMS): −31 ($\underline{Si}$Si). Elemental analysis: N 6.97% (calc. 7.18%); C 55.19% (calc. 55.40%); H 9.24% (calc. 8.72%).

RESULTS AND DISCUSSION

The most straightforward synthetic strategies towards such polymers imply the generation of *N*-methyl-2,5-dilithiopyrrole **2**, followed by its condensation with the appropriate chlorosilane. The first step, i.e. formation of a lithiated heterocyclic compound, is a well-documented fundamental process in organic synthesis[18–20]. However, in spite of the good to excellent results obtained for the monolithiation and capture with electrophiles of various *N*-protected pyrroles, we met with only limited success when we tried to apply the most widely used procedure, described by Chadwick and co-workers[21,22] and Hasan *et al.*[23], to the generation of the desired *N*-methyl-2,5-dilithiopyrrole **2** [equation (1)]. Extensive formation of this intermediate under the reaction conditions used cannot be excluded, but after treatment with trimethylsilyl chloride (TMSCl) the isolated crude product contained only a small amount of 2,5-bis(trimethylsilyl)-*N*-methylpyrrole, besides a larger quantity of the monosilylated compound. We suspect that the large



(1)



(2)

amount of tetramethylethylenediamine (TMEDA), necessary for the lithiation step, competes favourably with dilithiopyrrole **2** for TMSCl during the silylation step. Quite similar results were observed when using t-BuOK/t-BuLi as base system (in Et_2O at −78°C) for the lithiation of *N*-methylpyrrole.

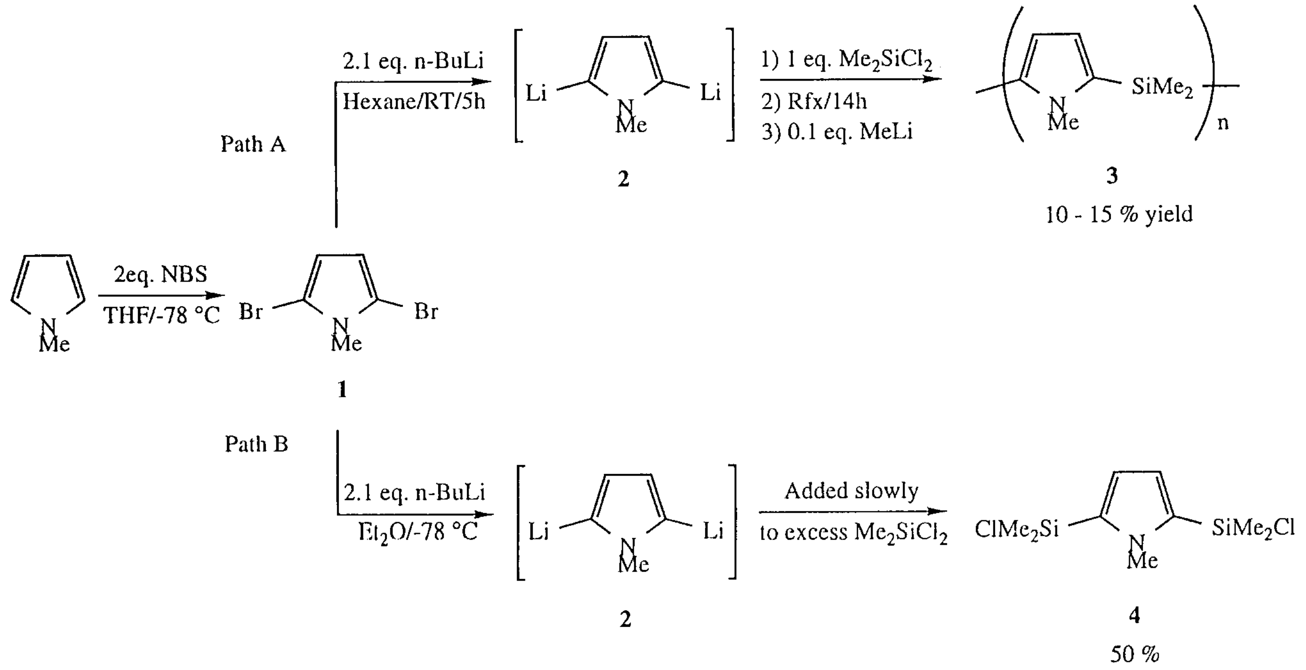
The second method, i.e. halogen–metal exchange, turned out to be much more successful for the generation of the desired dilithiopyrrole intermediate, although it adds another step (preparation of *N*-methyl-2,5-dibromopyrrole **1**) to the overall synthetic scheme. While the more traditional electrophilic halogenation reagents produce mixtures of halogenopyrroles in low yields[24], *N*-bromosuccinimide (NBS) has been reported to allow the clean and high yield synthesis of *N*-methyl-2-bromopyrrole (using 1 eq. NBS/THF/−78°C), as well as of *N*-methyl-2,5-dibromopyrrole **1** (using 2 eq. NBS/THF/−78°C) with excellent selectivities[25]. In a preliminary control experiment, and using this bromination protocol followed by Br/Li exchange (n-BuLi/Et_2O/−78°C) and reaction with Me_2HSiCl, we have prepared *N*-methyl-2,5-bis(dimethylhydrosilyl)pyrrole in 93% crude yield [equation (2)].

On the other hand, slow addition of **2** to a large excess of Me_2SiCl_2 in ether led to predominant formation of *N*-methyl-2,5-bis(dimethylchlorosilyl)pyrrole **4**, which was isolated by distillation in good yield (*Scheme 1*, Path B).

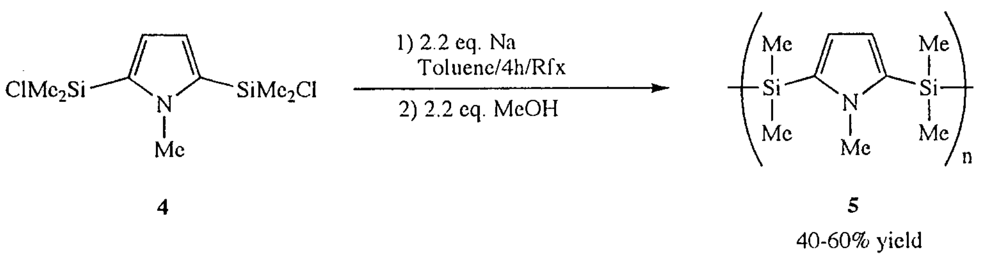
Polymer syntheses

On the basis of the above results, we have attempted to prepare poly[(dimethylsilylen)-*N*-methyl-2,5-pyrrolylene] **3** by slowly adding dimethyldichlorosilane to a suspension of *N*-methyl-2,5-dilithiopyrrole **2** in hexane (*Scheme 1*, Path A). After 14 h of gentle refluxing 0.1 eq. MeLi was added to eliminate the unreacted Si–Cl end groups[13,14]. Polymer **3** was obtained (hydrolytic work-up) by precipitation from THF by methanol in 11% yield.

On the other hand, from the *N*-methyl-2,5-bis(dimethylchlorosilyl)pyrrole **4**, we prepared the poly[(tetramethyldisilylen)-*N*-methyl-2,5-pyrrolylene] **5**, by



Scheme 1



Scheme 2

Table 1 M_w, heterogeneity from g.p.c. and yield of polymer **5** syntheses

Duration of synthesis (min)	M_w (PS equivalents)	Heterogeneity (M_w/M_n)	Yield (%)
90	7900	6.72	10.9
150	5900	1.79	27.5
240	6300	1.83	48.2
240	7100	2.39	61.3
240	5500	1.77	47.9
360	1400	2.28	40.1
360	6300	1.95	55.7

classical Wurtz synthesis (*Scheme 2*). Owing to slow degradation of the monomer **4**, the different polymer syntheses reported in *Table 1* were performed using a freshly prepared monomer batch.

Spectroscopic characterizations of polymer 5

The ^{1}H n.m.r. spectrum of polymer **5** is reproduced in *Figure 1*. Three main peaks are observed: the most shielded one (0.3 ppm) is assigned to the methyls on Si and the following one (around 3.4 ppm) to the methyls on nitrogen. The less shielded peak (>6 ppm) corresponds to the aromatic protons in 3 and 4 positions on the pyrrole ring. All the corresponding protons of the

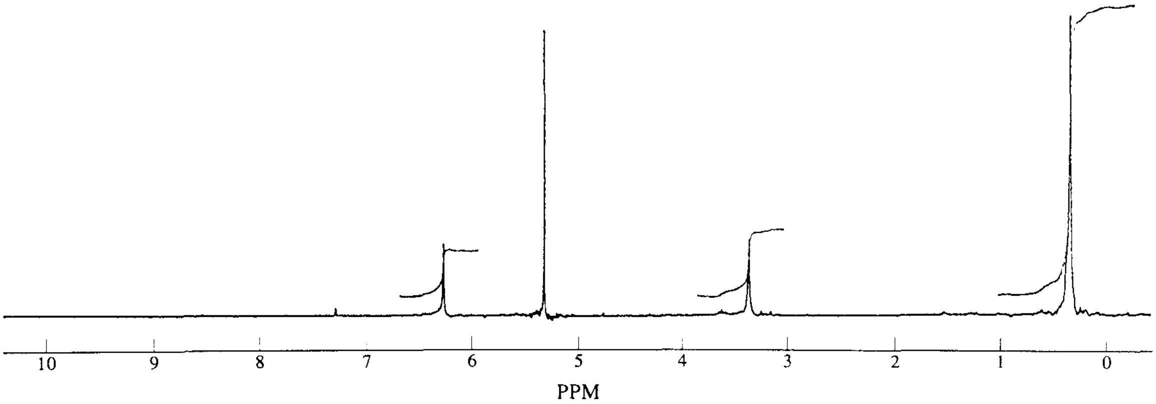


Figure 1 ^{1}H n.m.r. spectrum of poly(tetramethyldisilylen)-*N*-methyl-2,5-pyrrolylene (CH_2Cl_2 as reference: $\delta = 5.3$ ppm)

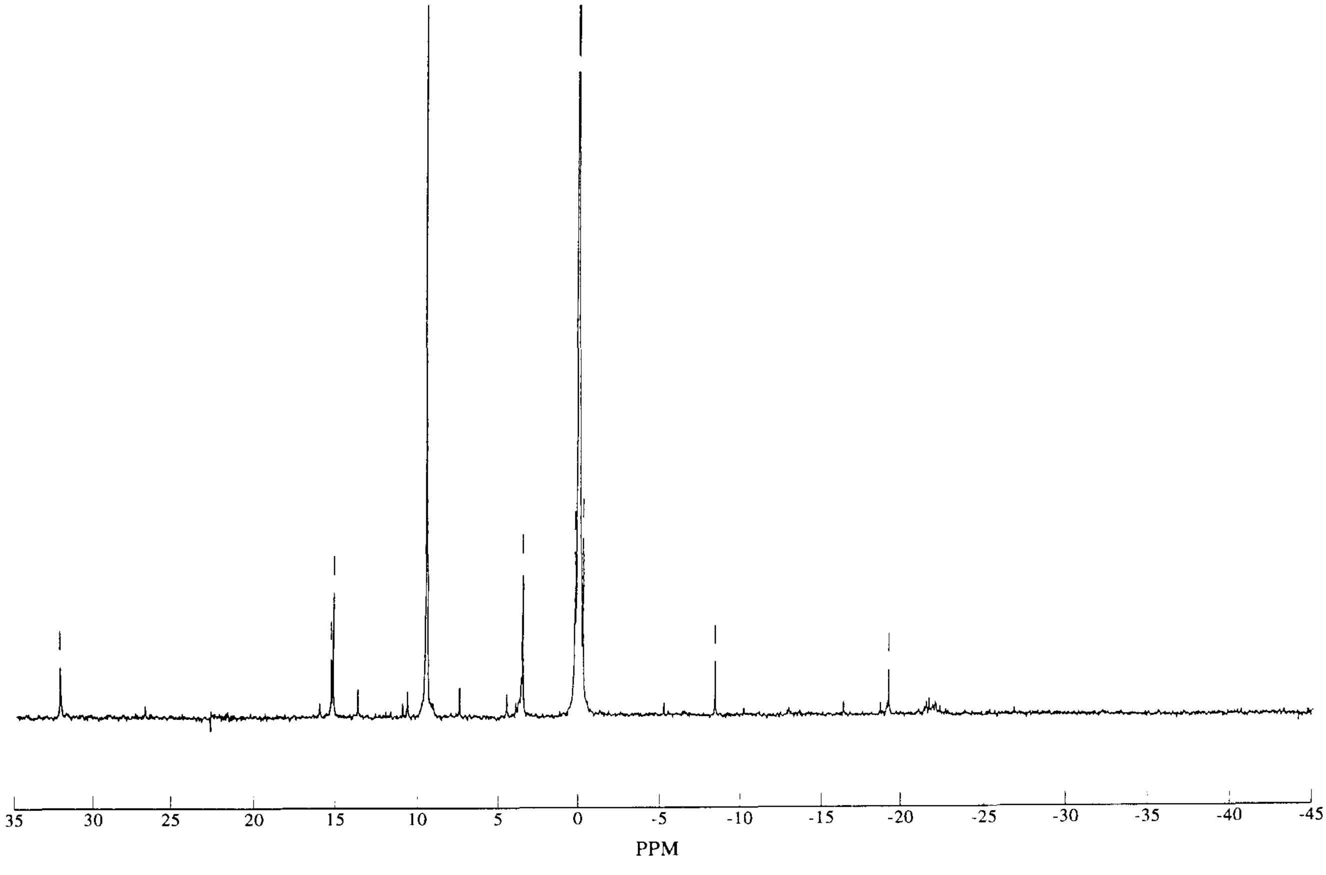


Figure 2 ^{29}Si n.m.r. spectrum of *N*-methyl-2,5-bis(dimethylchlorosilyl)pyrrole. (TMS as reference: $\delta = 0$ ppm)

monomer **4** are less shielded owing to the deshielding effect of the Cl atoms.

The ^{29}Si n.m.r. spectra of monomer **4** and polymer **5** are presented in *Figures 2* and *3* respectively. Besides the TMS reference peak (0 ppm), the main peak in the monomer spectrum is found at +9.3 ppm due to the deshielding effect of the Cl atoms[26]. Other peaks should be assigned to silicon-containing impurities. Among them, the +3.8 ppm peak is probably due to a siloxane –SiO– arising from a limited hydrolysis. In the spectrum of polymer **5**, no more peaks can be found in the +10 ppm area, witnessing the disappearance of all SiCl groups. Correspondingly, a strong peak is found at −31 ppm. By analogy with classical polysilane spectra[26], it should be assigned to disilylene –SiSi– silicon atoms. A weak peak around +2 ppm is probably due to –Si–O–CH_3 end groups. Other weak peaks remain unassigned and arise probably from impurities.

Due to some unavoidable degradation in air, the *FT*i.r. spectrum of monomer **4** showed strong peaks assigned to siloxane –SiO– links and is therefore not reported. The *FT*i.r. spectrum of polymer **5** shows absorption bands at 2955 and 2896 cm^{-1} due to asymmetrical and symmetrical stretchings of CH_3. Two CH_3 bands are also found at 1347 and 1328 cm^{-1} which are to be assigned to methyls linked to nitrogen and silicon, respectively. Stretchings of CH on pyrrole give rise to the 3117 cm^{-1} band, while ring stretching bands (breathing bands) occur at 1474, 1401 and probably as a shoulder at 1510 cm^{-1}. Bands at 1282, 1175 and 916 cm^{-1} also arise from pyrrole CH vibrations. Out-of-plane deformation bands of pyrrole are reported to arise in the 1000–700 cm^{-1} region[27]. In poly[(tetramethyldisilylen)-*N*-methyl-2,5-pyrrolylene] **5**, this band can be found at around 800 cm^{-1}. The SiSi–CH_3 band appears at 1245 cm^{-1}, in a position previously reported for polysilanes[28]. A shoulder at 1257 cm^{-1} can be assigned to OSi–CH_3 (ref. 28), indeed the corresponding Si–CH_3 band is observed at 1261 cm^{-1} in the hydrolysed monomer. Similarly, two bands at 1078 and 1022 cm^{-1} can be assigned to siloxane Si–O–Si links which appear as broad bands in the hydrolysed monomer. Nevertheless, some Si–O links in the polymer could also arise from Si–O–CH_3 end groups.

In the u.v. spectra of monomer **4** and polymer **5** an absorption band is observed around 230 nm, but, in the polymer spectrum, an additional, more intense band is seen at 266 nm. This bathochromic effect is probably due to the so-called electron σ delocalization, as observed in polysilane spectra[29]. It is well known that the bathochromic effect is enhanced by the length of the Si–Si chain. In polymer **5**, only two silicon atoms are involved in this delocalization, explaining the relatively low bathochromic shift. A longer polysilane chain between the aromatic rings should increase the bathchromic effect.

Polymer molecular characterizations

Poly[(dimethylsilylen)-*N*-methyl-2,5-pyrrolylene] **3** was analysed by g.p.c. with polystyrene calibration

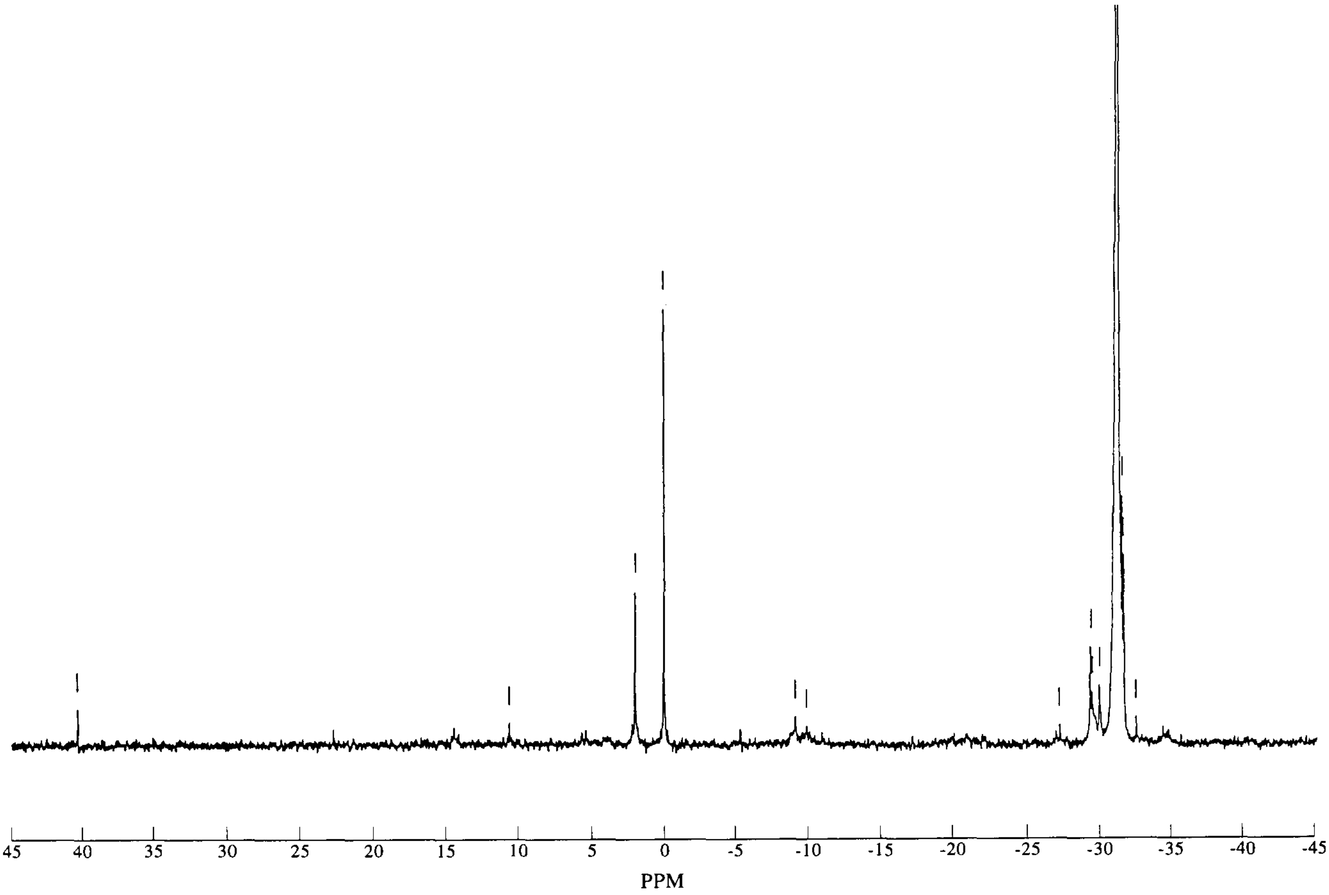
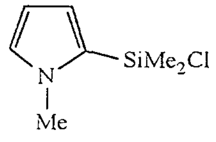


Figure 3 ^{29}Si n.m.r. spectrum of poly(tetramethyldisilylen)-*N*-methyl-2,5-pyrrolylene (TMS as reference: $\delta = 0$ ppm)

$M_n = 1492$, $M_w = 1944$. This result, corresponding to oligomers, is not surprising owing to the synthesis procedure which requires, as any polycondensation, a perfect balance between monomers. This is particularly difficult in the present case, due to the high reactivity of *N*-methyl-2,5-dilithiopyrrole **2**. No improvement of the molecular weight has been attempted so far.

Poly[(tetramethyldisilylen)-*N*-methyl-2,5-pyrrolylene] **5** was also analysed by g.p.c. with polystyrene calibration. Results from seven different syntheses are reported in *Table 1*. It is to be noticed that each result is obtained starting from a freshly synthesized batch of monomer **4**. *Table 1* shows that, whatever the duration of the synthesis between 90 and 360 min, limited variations in molecular weight are observed. On the contrary, the yield increases significantly up to a reaction time of about 240 min. Modification of temperature, by using ethylbenzene (b.p. 136°C) instead of toluene (b.p. 110°C), does not modify synthesis results. Increasing the monomer concentration was also attempted, in order to modify the diffusion of reacting species to and from the sodium surface[30], but the only result was a strong decrease of the yield. The purity of the monomer **4** was therefore questioned. Indeed, g.c./m.s. analysis revealed the presence of several impurities, among them a few percent of *N*-methyl-2-(dimethylchlorosilyl)pyrrole **6**:



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This monofunctional species can be considered as responsible for the limited molecular weight values reported in *Table 1*. A second distillation of the monomer **4** succeeded in eliminating most of the impurities except for the monofunctional species **6**, resulting in a limited improvement in molecular weight (7800 after 240 min). Further progress in monomer purification will be necessary to reach higher molecular weight polymers **5**.

CONCLUSIONS

Synthesis of first members of a series of 'mixed' polysilanes was attempted on the basis of *N*-methyl-2,5-pyrrolylene and dimethylsilylene units. As a first step, the synthesis of *N*-methyl-2,5-dilithiopyrrole **2** was successfully achieved in two steps: 2,5-bromination of *N*-methylpyrrole by *N*-bromosuccinimide, followed by dilithiation using n-BuLi. *N*-Methyl-2,5-bis(dimethylchlorosilyl)pyrrole **4** was also successfully synthesized by adding a large excess of Me_2SiCl_2.

Poly[(dimethylsilylen)-*N*-methyl-2,5-pyrrolylene] **3** was synthesized by equimolar reaction between **2** and Me_2SiCl_2, while poly[(tetramethyldisilylen)-*N*-methyl-2,5-pyrrolylene] **5** was synthesized by Wurtz coupling of *N*-methyl-2,5-bis(dimethylchlorosilyl)pyrrole **4**. Optimization of molecular weight and yield of the latter polymer **5** was attempted by modifying reaction duration, temperature and monomer concentration. However, the main parameter governing the final molecular weight appeared to be the monomer purity. Work is in progress to obtain monomer of higher purity, leading to high molecular weight polymer.

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REFERENCES

1 'Silicon Based Polymer Science' (Eds. J. M. Zeigler and F. W. G. Fearon), American Chemical Society, Washington, DC, 1990

2 'Organosilicon Chemistry: From Molecules to Materials' (Eds N. Auner and J. Weis), VCH, Weinheim, 1994

3 Ishikawa, M., Hasegawa, Y., Hatano, T., Kunai, A. and Yamanaka, T. *Organometallics* 1989, **8**, 2741

4 Ishikawa, M., Hasegawa, Y., Kunai, A. and Yamanaka, T. *J. Organomet. Chem.* 1990, **381**, C57

5 Ijadi-maghsoodi, S. and Barton, T. J. *Macromolecules* 1990, **23**, 4485

6 Ijadi-maghsoodi, S., Pang, Y. and Barton, T. J. *J. Polym. Sci. (A), Polym. Chem.* 1990, **28**, 955

7 Corriu, R. J. P., Gueri, C., Henner, B., Kuhlmann, T., Jean, A., Garnier, F. and Yassar, A. *Chem. Mater.* 1990, **2**, 351

8 Corriu, R. J. P., Gueri, C., Henner, B., Jean, A. and Mutin, H. *J. Organomet. Chem.* 1990, **396**, C35

9 Corriu, R. J. P., Gerbier, P., Gueri, C. and Henner, B. *Angew. Chem. Int. Ed. Engl.* 1992, **31**, 1195

10 Corriu, R. J. P., Douglas, W. E. and Yang, Z.-X. *J. Polym. Sci. (C), Polym. Lett.* 1990, **28**, 431

11 Oshita, J., Ohsaki, H. and Ishikawa, M. *Bull. Chem. Soc. Jpn* 1993, **66**, 1795

12 Imori, T., Woo, H.-G., Walzer, J. F. and Don Tilley, T. *Chem. Mater.* 1993, **5**, 1487

13 Chicart, Ph., Corriu, R. J. P., Moreau, J. J. E., Garnier, F. and Yassar, A. *Chem. Mater.* 1991, **3**, 8

14 Chicart, Ph., Corriu, R. J. P., Moreau, J. J. E., Garnier, F. and Yassar, A. in 'Inorganic and Oragnometallic Polymers with Special Properties' (Ed. R. M. Laine), Kluwer Academic Publishers, Dordrecht, 1992, p. 179

15 Nguyen, M. T., Diaz, A. F., Dement'ev, V. V. and Pannell, K. H. *Chem. Mater.* 1993, **5**, 1389

16 Foucher, D. A., Ziembinski, R., Tang, B.-Z., Macdonald, P. M., Massey, J., Jaeger, C. R., Vancso, G. J. and Manners, I. *Macromolecules* 1993, **26**, 2878

17 Rulkens, R., Lough, A. J. and Manners, I. *J. Am. Chem. Soc.* 1994, **116**, 797

18 Gschwend, H. W. and Rodriguez, H. R. in 'Organic Reactions', John Wiley & Sons, New York, 1979, Vol. 26, p. 1

19 Wakefield, B. J. 'Organolithium Methods', Academic Press, Harcourt Brace Jovanovich Publishers, London, Benchtop Edition, 1990

20 Snieckus, V. *Chem. Rev.* 1990, **90**, 879

21 Chadwick, D. J. and Willbe, C. *J. Chem. Soc. Perkin I* 1977, 887

22 Chadwick, D. J. and Cliffe, I. A. *J. Chem. Soc. Perkin I* 1979, 2845

23 Hasan, I., Marinelli, E. R., Chang lin, L.-C., Fowler, F. W. and Levy, A. B. *J. Org. Chem.* 1981, **46**, 157

24 Cordell, G. A. *J. Org. Chem.* 1975, **40**, 3161, and refs cited therein

25 Gilow, H. M. and Burton, D. E. *J. Org. Chem.* 1981, **46**, 2221

26 de Mahieu, A.-F. 'Synthèse et caractérisation de polysilanes et de copolysilanes', *PhD Thesis*, Louvain-la-Neuve, 1993

27 Bellamy, L. J. 'The Infrared Spectra of Complex Molecules', 3rd Edn, Chapman and Hall, London, 1975

28 Devaux, J., Sledz, J., Schué, F., Giral, L. and Naarman, H. *Makromol. Chem.* 1990, **191,** 139

29 West, R., David, L. D., Djurovitch, P. I., Stearly, K. L., Srinivasan, K. S. U. and Yu, A. *J. Am. Chem. Soc.* 1981, **103,** 7352

30 Zeigler, J. M., Harrah, L. A. and Johnson, A. W. *Polym. Prepr.* 1981, **28,** 424