Eur. Polym. J. Vol. 21, No. 3, pp. 301-308, 1985
Printed in Great Britain. All rights reserved

0014-3057/85 $3.00 + 0.00
Copyright © 1985 Pergamon Press Ltd

SYNTHESIS OF POLY(SULPHONE-*b*-SILOXANE)S — III

SYNTHESIS OF POLY(SULPHONE-*b*-SILOXANE) BY REACTION OF α,ω-DIALLYL OLIGOSULPHONES WITH α,ω-DISILANE OLIGOSILOXANES

D. GAGNEBIEN, P. J. MADEC and E. MARÉCHAL
Laboratoire de Synthèse Macromoléculaire (LA 24, CNRS), Université Pierre et Marie Curie, 12 rue Cuvier, 75005 Paris, France

(*Received* 18 *July* 1984)

Abstract—Block copolycondensation of α, ω-diallyl oligosulphones with α, ω-disilane oligosiloxanes, has been studied on models and on oligomers. Poly(bisphenol *A*-*b*-siloxane) and poly(sulphone-*b*-siloxane)s were prepared and thoroughly characterized. GPC, ^{1}H-NMR and ^{13}C-NMR show that the blocking reaction took place. The chain length was limited by stirring difficulties.

INTRODUCTION

In the first part of this series [1] we reported the results of a fundamental study of the epoxy-phenol reaction when carried out on models; they were used to prepare various copolymers associating oligosiloxane and oligosulphone blocks or one of these blocks with the model of the other. The molecular weights of the copolymers containing polysulphone blocks were limited by the difficulty of obtaining high extents of reaction, shown to be due to the complete incompatibility of the two oligomers. We now study the block polycondensation of α,ω-diallyl oligosulphones (APS) with α,ω-disilane oligodimethyloxanes (HPSi).

EXPERIMENTAL

Synthesis

α, ω-Diallyl oligosulphones. PhPS ($\bar{M}_n$ = 1500; 1500 g; 1 mol) was dissolved in diethyleneglycol (diglyme) by heating this solvent under N_2 to refluxing (162°). Freshly distilled DMDA (10.65 g; 0.05 mol) was added and the temperature maintained at 145°; AEP (228 g; 2 mol) was added dropwise. The reaction was carried out at 145° for 6 hr.

Poly(BPA-b-Si). A mixture of ABPA (45.6 g; 0.1 mol) and H_2PtCl_6 (1% by weight; from a 0.1% *t*-butanol solution) was heated to 120°; HPSI ($\bar{M}_n$ = 1200; 120 g; 0.1 mol) was then introduced by successive additions. After each addition, the reaction mixture became opaque but cleared rapidly; its viscosity increased progressively; the reaction carried out for 24 hr led to a highly viscous and uncoloured resin.

Poly(S-b-Si). A mixture of APS3 ($\bar{M}_n$ = 1700; 173 g; 0.1 mol), diglyme (80 ml) and H_2PtCl_6 (1% by weight from a 0.1% *t*-butanol solution) was heated to 120° and this temperature was maintained for the whole time of reaction. HPSi ($\bar{M}_n$ = 1200; 120 g; 0.1 mol) was added in small portions: after each addition demixing took place, then slowly disappeared; when the mixture became homogeneous, another fraction was added. After the last addition, the reaction was continued until the viscosity of the medium became too high to permit stirring.

Purification of the product: the copolymer (50 g) was dissolved in CH_2Cl_2 (100 ml) then precipitated in boiling methanol (100 ml), filtered and vacuum dried (1 Torr; 100°; 24 hr).

Analysis

As in part II [2].

SYNTHESIS AND CHARACTERIZATION OF THE OLIGOMERS

α,ω-Disilane oligosiloxanes HPSi and α,ω-diphenololigosulphones (PhPS) were described in part II [2].

We prepared APS by reacting PhPS with 1-allyloxy-2,3-epoxy propane (AEP) [3]. To avoid branching reactions, which would lead to oligomers with functionality >2, we carried out the reaction at the stoichiometry of the reactants. Since, unlike BPA, polysulphones are not soluble in AEP, it is necessary to add a solvent which can be the dimethylether of diethyleneglycol (see Experimental section); as with the model reactions [1], we used dimethyldodecylamine (DMDA) as catalyst.

As in part II [2], we characterized these oligomers by several techniques.

^{1}H-NMR (250 MHz)

The spectra relative to the chain terminations are reported in Fig. 1. The characteristics of the precursors: PhPS1 ($\bar{M}_n \simeq$ 700) PhPS3 ($\bar{M}_n \simeq$ 1500), PhPS6 ($\bar{M}_n \simeq$ 2800) are reported in Table 3 of the second part of this series [2]. ABPA is the diallyether of bisphenol *A* [1]. In the case of APS, we succeeded in determining the functionality *f* by comparing the integrations of the end-group protons with those of the aromatic or the isopropylic protons of the chain: $1.9 < f < 2.0$. This functionality is purely allylic, as there is no signal corresponding to an epoxidic structure in the spectrum.

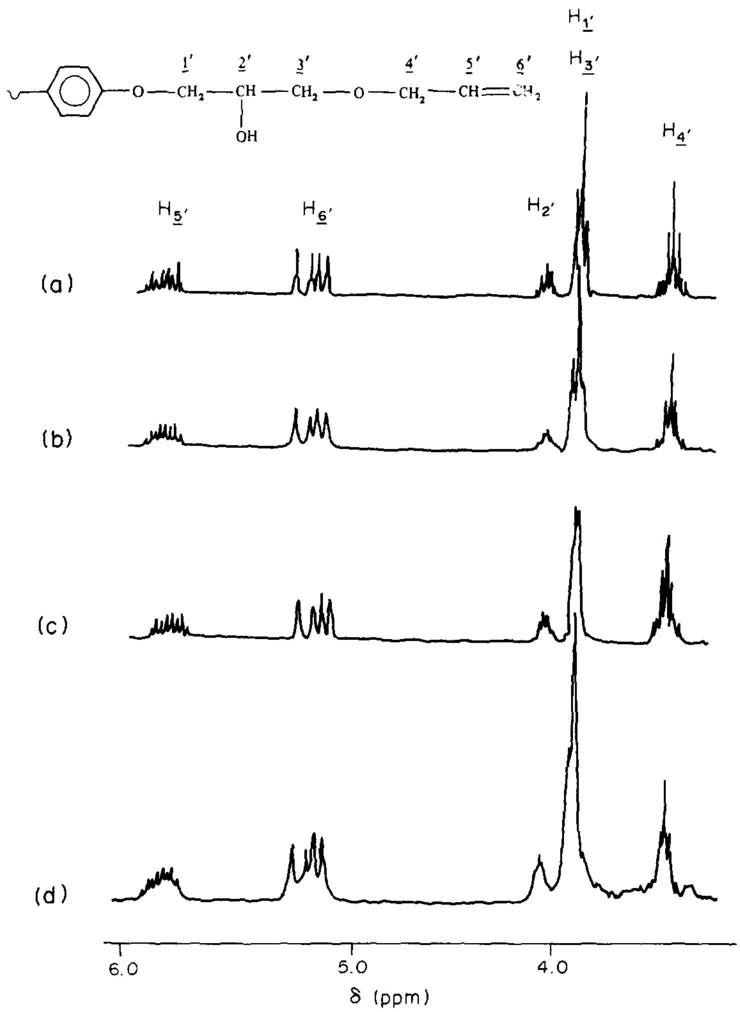


Fig. 1. ^{1}H-NMR spectra (250 MHz) of α,ω-diallyl oligosulphones: (a) ABPA; (b) APS1; (c) APS3; (d) APS6. For notations (see text).

^{13}C-NMR (60.83 MHz)

The spectra for PhPS3 and APS3 are reported in Fig. 2 and Table 1. Their comparison shows that APS3 does not contain residual phenolic (154.0 ppm) and epoxidic (43.5 and 50.1 ppm) groups. Phenolic carbon 1 is completely etherified and the signal corresponding to carbon 4 is slightly shifted. As for ABPA (see part I [1]), the 4 carbons α to an oxygen atom (1', 2', 3', 4') give a pattern of 3 peaks (the signals corresponding to carbons 1' and 2' are at exactly the same place).

GPC

Chromatograms of APS are practically similar to those of PhPS; only compounds of low molecular weights show new distributions due to endgroups contribution.

Table 1. ^{13}C characteristics of the end-groups of PhPS and APS (numbering in Fig. 1)

Number of carbon	Before modification (δ ppm)	Number of carbon	After modification (δ ppm)
1	153.6	1	156.6
4	142.1	4	142.9
1'	43.5	1'	69.0
2'	50.1_5	2'	69.0
3'	70.3	3'	71.0
4'	71.6	4'	72.1
5'	134.0	5'	134.3
6'	116.3	6'	117.0

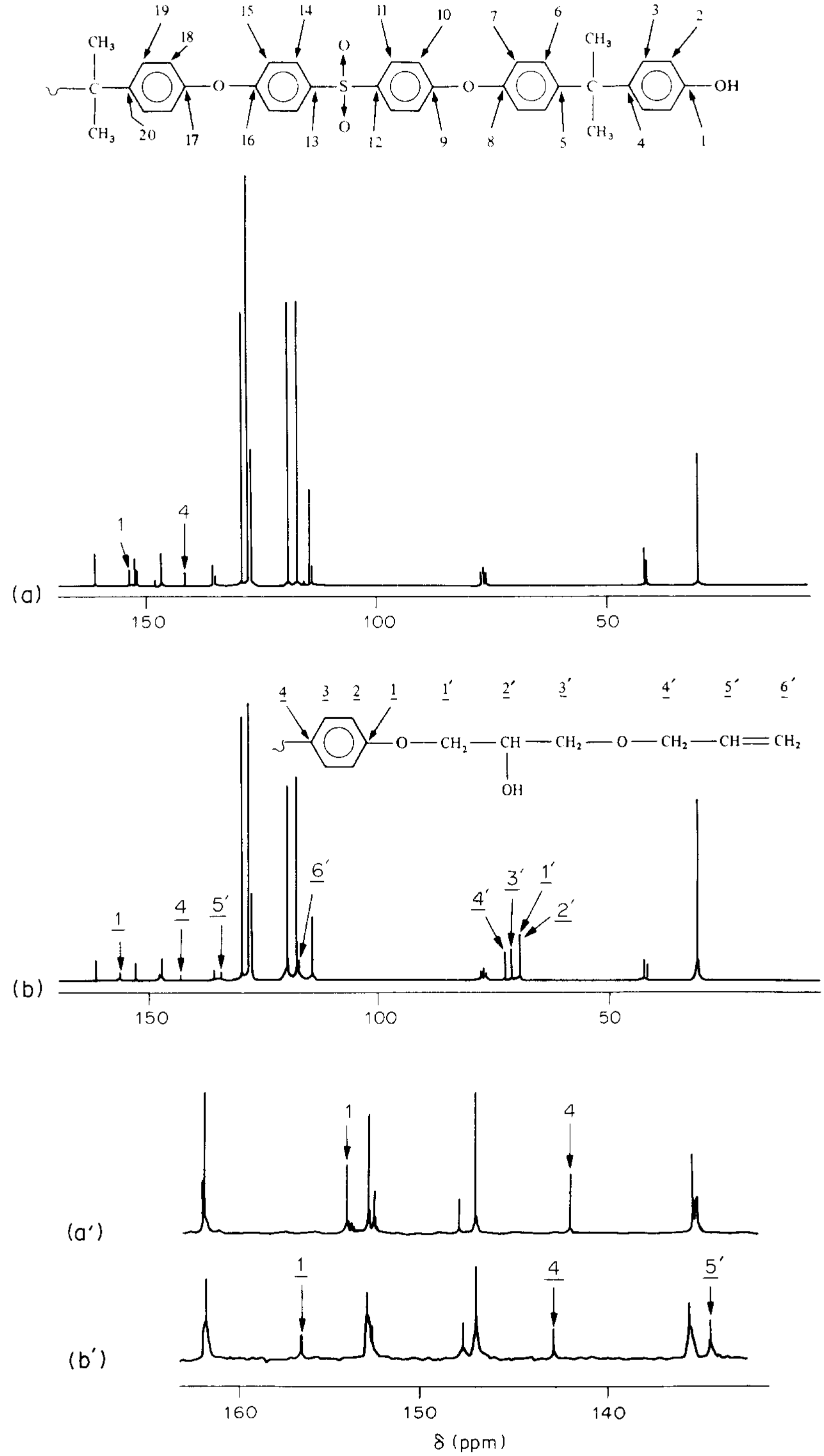


Fig. 2. ^{13}C-NMR spectra of PhPS3 (a) and APS3 (b). (a') and (b') result from an enlargement of the 130–165 ppm parts of spectra (a) and (b).

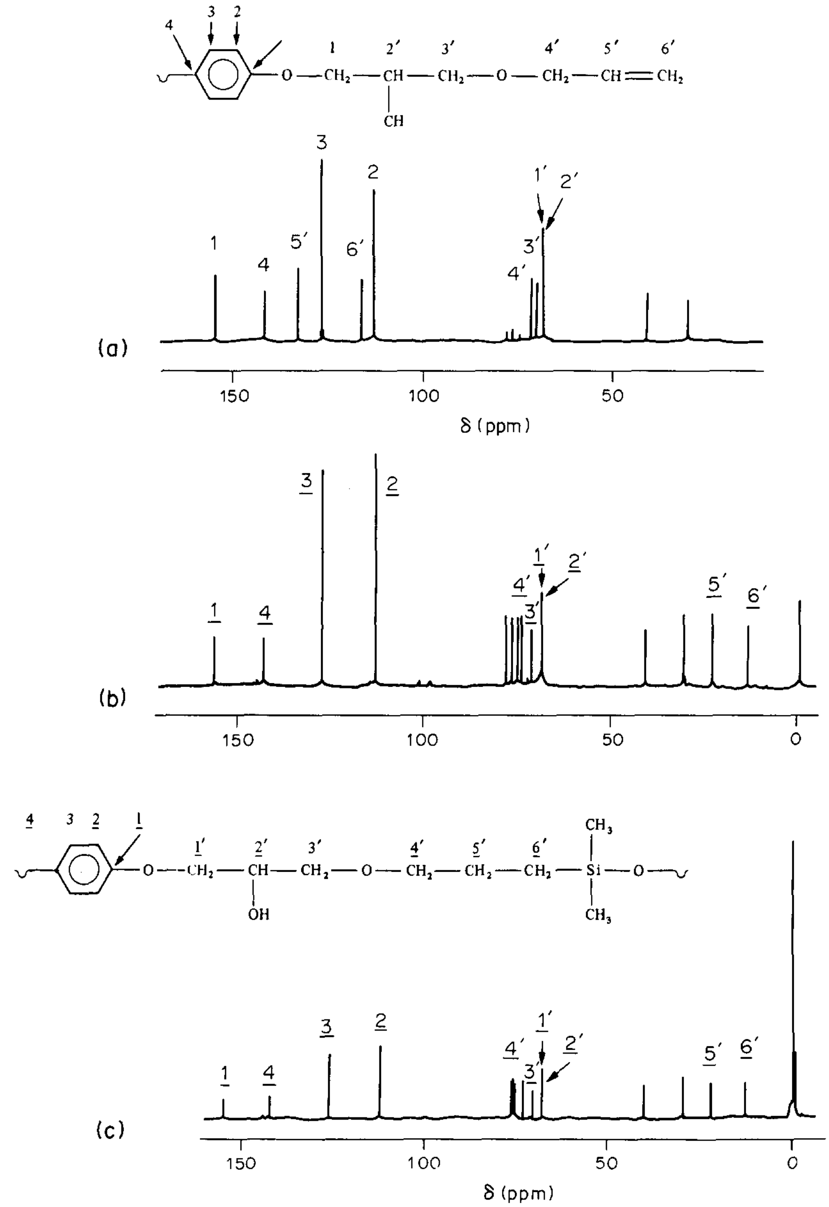
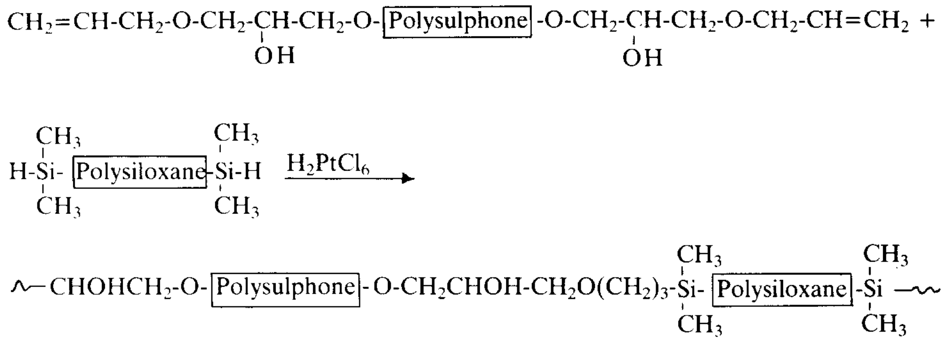


Fig. 3. ^{13}C-NMR (20.13 MHz) of ABPA (a), poly(BPA-TSi) (b) and poly(BPA-*b*-PSi) (c). Solvent $CDCl_3$.

SYNTHESIS OF THE POLY(SULPHONE-*b*-SILOXANE)S

These materials are synthesized according to the reaction:



$$CH_2{=}CH\text{-}CH_2\text{-}O\text{-}CH_2\text{-}\underset{\displaystyle OH}{CH}\text{-}CH_2\text{-}O\text{-}\boxed{\text{Polysulphone}}\text{-}O\text{-}CH_2\text{-}\underset{\displaystyle OH}{CH}\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH{=}CH_2 +$$

$$H\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}\boxed{\text{Polysiloxane}}\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}H \xrightarrow{H_2PtCl_6}$$

$$\sim CHOHCH_2\text{-}O\text{-}\boxed{\text{Polysulphone}}\text{-}O\text{-}CH_2CHOH\text{-}CH_2O(CH_2)_3\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}\boxed{\text{Polysiloxane}}\text{-}\overset{CH_3}{\underset{CH_3}{Si}} \sim$$

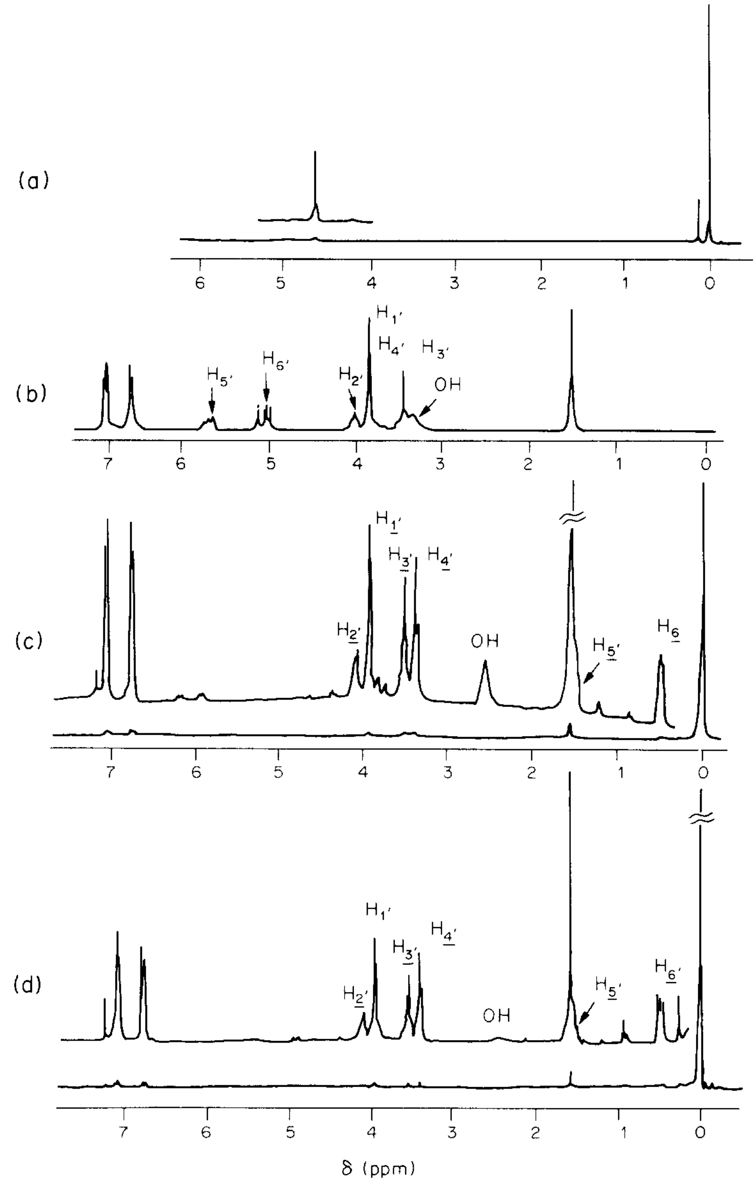


Fig. 4. ^{1}H-NMR spectra (250 MHz) of HPSi1 (a), ABPA (b), poly(BPA-*b*-TSi) (c) and poly(BPA-*b*-PSi) (d). Solvent = $CDCl_3$.

Hydrosilylation is the subject of many fundamental and applied studies and has been used to prepare block copolymers [4,5] or crosslinked materials [6]. Several fundamental studies concern the catalyst [7–11] and the possible side reactions [12,13]; however when reactants are polymers, the contribution of side reactions is very low.

Coupling of α,ω-diallyl bisphenol A (ABPA) with α, ω-disilane polydimethylsiloxanes (HPSi)

The reaction was carried out in the melt; however, in the case of tetramethyldisiloxane (HTSi), the reaction temperature was kept below 40–50° due to the high volatility of this reactant.

HPSi or HTSi was added progressively (see Experimental section); after each addition the reaction mixture became cloudy as the two reactants are not compatible; however it cleared rapidly as the reaction progressed.

The reaction product is soluble in the solvents for the two reactants. Its gel permeation chromatogram shows a net increase of the molecular weight: poly (BPA-$\underline{b}$-TSi) ($\bar{M}_n$ = $\underline{4500}$) $\bar{DP}_n$ = 7.6) poly(BPA-*b*-PSi) ($\bar{M}_n$ = 6000) $\bar{DP}_n$ = 4.0). However due to calibration difficulties (see part II), these values are only indicative.

^{13}C-NMR spectra of ABPA (a) and of its reaction products with HTSi (b), and HPSi (c) are reported in Fig. 3. (b) and (c) are very similar and show that carbons 5′ and 6′ of allyl group are no longer present and are replaced by methylenic carbons $\underline{5}'$ and $\underline{6}'$ close to the silicon atom. A slight deshielding of methylenic carbons $\underline{4}'$ is observed; it is more important in the case of TSi than in that of PSi. The characteristics of the carbons relative to the junction are reported in Table 2.

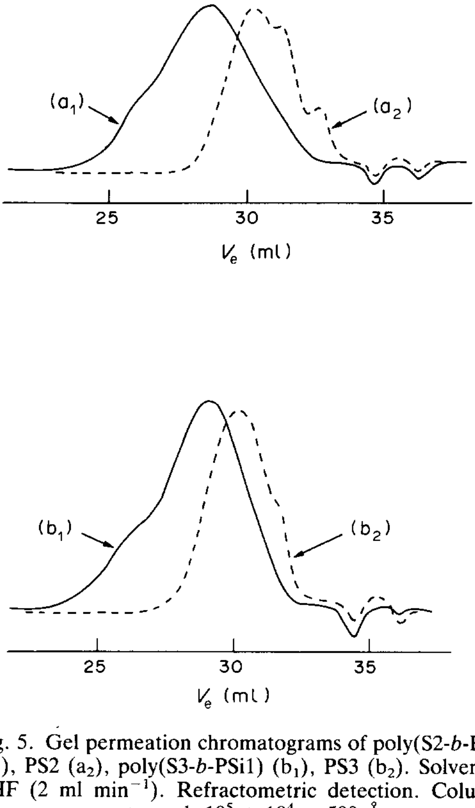


Fig. 5. Gel permeation chromatograms of poly(S2-*b*-PSil) (a_1), PS2 (a_2), poly(S3-*b*-PSil) (b_1), PS3 (b_2). Solvent = THF (2 ml min^{-1}). Refractometric detection. Columns μ-styragel: 10^5 + 10^4 + 500 Å.

The ^{1}H-NMR spectra of an α, ω-disilane oligosiloxane HPSil (a), of ABPA (b), poly(BPA-*b*-TSi) (c) and poly(BPA-*b*-PSi) are reported in Fig. 4. These spectra are very similar to those of the block copolymers obtained by epoxy-phenol reaction (part II). Methylenic protons $\underline{4}'$, $\underline{5}'$ and $\underline{6}'$ give peaks at 0.5, 1.55 and 3.4 ppm.

Table 2. ^{13}C characteristics of the carbons 1′ to 6′ in ABPA (a) and in poly(BPA-*b*-TSi) (b) and poly(BPA-$\bar{b}$-PSi) (c) (Ref. TMS; numbering as in Fig. 3)

Number of carbon	δ ppm/TMS(a)	Number of carbon	δ ppm/TMS(b)	δ ppm/TMS(c)
1′	68.7	$\underline{1}'$	69.0	69.0
2′	68.5_5	$\underline{2}'$	69.0	69.0
3′	70.7	$\underline{3}'$	71.5	71.4
4′	71.9	$\underline{4}'$	74.2	73.1
5′	134.2	$\underline{5}'$	23.3	23.3
6′	116.7_5	$\underline{6}'$	14.1	14.1

Coupling of α,ω-diallyl oligosulphones (APS) with α, ω-disilane polydimethylsiloxanes (HPSi)

As with the systems ABPA–TSi and ABPA–PSi, the reaction was carried out in dimethylic ethers of ethylene or diethylene glycols, as separation takes place. It was however more important than in the case of the systems ABPA–HTSi and ABPA–HPSi. Only very small quantities of solvent are required; after each addition of HPSi, the reaction mixture became heterogeneous and then homogeneous at which time another addition was made (see Experimental section). The reaction was carried out until the mixture was too viscous for efficient stirring.

The GPC chromatograms are reported in Fig. 5; they show a net increase of molecular weights: poly(S2-*b*-PSi 1) ($\bar{M}_n$: 5500; $\bar{DP}_n$: 2.5); poly(S3-*b*-PSi 1) ($\bar{M}_n$: 5000; $\bar{DP}_n$: 2.0); as in part II of this series [2] these values must be accepted with some reserve since the calibration by oligosulphones causes problems in the case of copolymers.

^{13}C-NMR spectra relative to the polycondensation of an oligosulphone APS 2 ($\bar{M}_n \simeq 1300$) with an oligosiloxane HPSi 1 ($\bar{M}_n \simeq 1200$) are reported in Fig. 6. There are no peaks corresponding to allylic protons in poly(S2-*b*-PSi); on the other hand, methylenic protons give peaks at 14 and 23 ppm. As in the spectra of the copolymers obtained by epoxyphenol reaction, a slight deshielding of proton $\underline{4}'$ is observed.

^{1}H-NMR spectra of the various copolymers are similar to that of poly(S2-*b*-PSi 1) (Fig. 7); allylic protons (5.15 and 5.85 ppm) are no longer present and methylenic protons of the junction give peaks at 1.5 ppm ($H_{5'}$) and 0.45 ppm ($H_{6'}$). As with NMR spectra, these are exactly similar to the spectra of the compounds obtained by epoxy-phenol reaction.

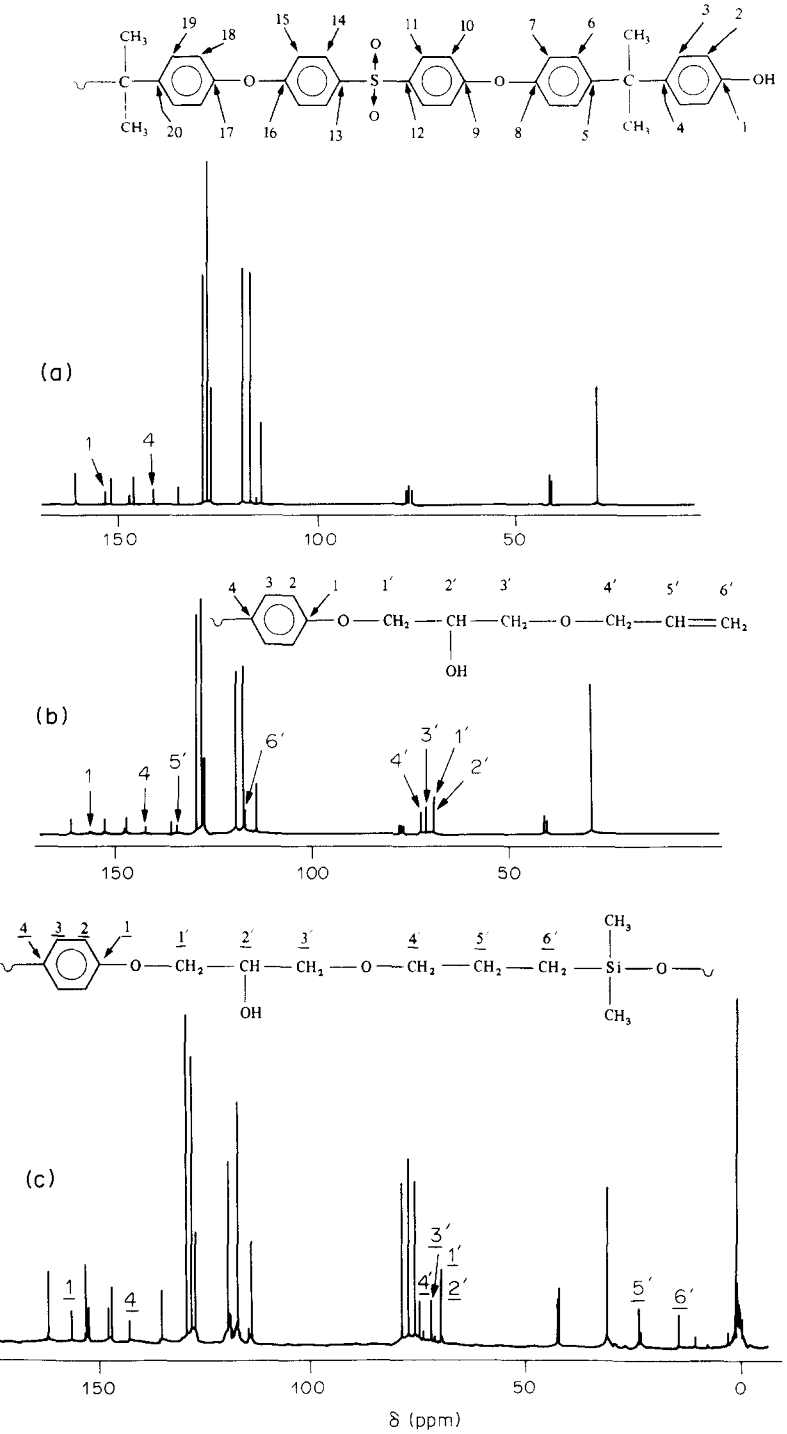


Fig. 6. ^{13}C-NMR spectra of PhPS2 (a), APS2 (b) and poly(S2-*b*-PSi) (c). Solvent = CDCl$_3$.

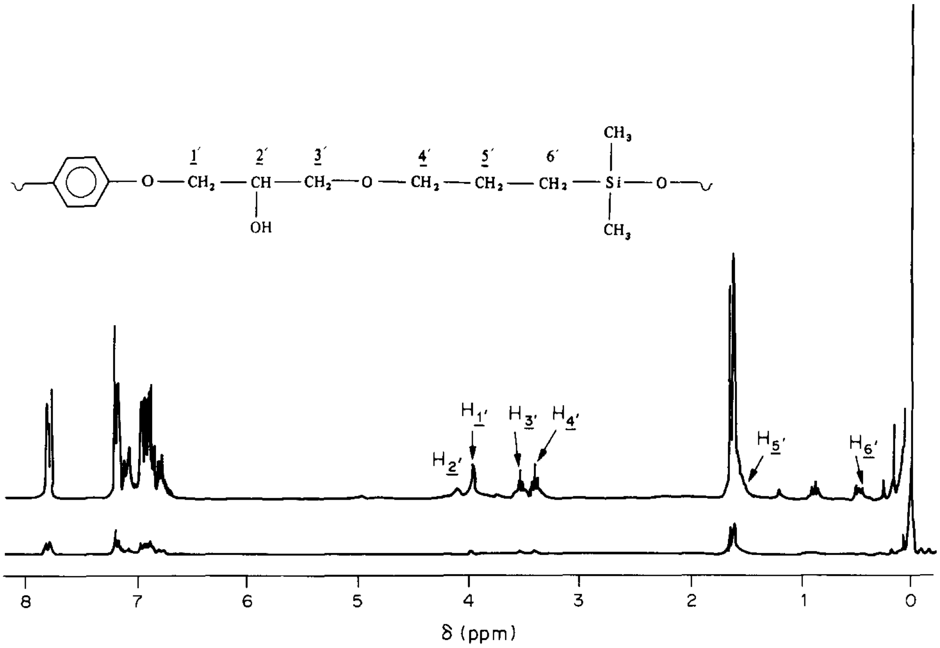


Fig. 7. ^{1}H-NMR spectrum (250 MHz) of poly(S2-*b*-PSi). Solvent = $CDCl_3$.

CONCLUSION

Poly(sulphone-*b*-siloxane) with Si-C junctions and side hydroxygroups were obtained. All analyses (GPC, ^{13}C-NMR and ^{1}H-NMR) show that the blocking reaction took place. However, the chain length of the copolymers are limited by the extent of the reaction which stops when the medium becomes too viscous for efficient stirring. The same phenomenon was observed for the copolymers prepared by the epoxy-phenol reaction. This difficulty could be overcome in two ways, *viz*:

(a) optimization of the respective concentrations of the solvent and of the oligomers, in order to associate a low phase-segregation with a sufficiently high reactive group-concentration;

(b) post-treatment of these low molecular weight copolymers in a double screw extruder.

REFERENCES

1. D. Gagnebien, P. J. Madec and E. Maréchal, *Eur. Polym. J.* **21**, 273 (1985).
2. D. Gagnebien, P. J. Madec and E. Maréchal, *Eur. Polym. J.* **21**, 289 (1985).
3. F. Laval, P. J. Madec and E. Maréchal, *Fr. Demande* 8203522 (1982).
4. P. Chaumont, G. Beinert, J. Herz and P. Rempp, *Polymer* **22**, 663 (1981).
5. M. Galin and E. Mathis, *Makromolek. Chem.* **14**, 677 (1981).
6. G. Friedmann, J. Herz and J. Brossas, *Polym. Bull.* **6**, 251 (1982).
7. N. H. Sommers, E. W. Pietrusza and F. C. Whitmore, *J. Am. chem. Soc.* **69**, 188 (1947).
8. J. L. Speier, R. Zimmerman and J. A. Webster, *J. Am. chem. Soc.* **78**, 2278 (1956).
9. J. L. Speier, J. A. Webster and G. H. Barnes, *J. Am. chem. Soc.* **79**, 974 (1957).
10. G. Greber, *Angew. Makromolek. Chem.* **415**, 212 (1968).
11. A. J. Chalk and J. F. Harrod, *J. Am. chem. Soc.* **87**, 16 (1965).
12. P. Chaumont, G. Beinert, J. Herz and P. Rempp, *Eur. Polym. J.* **15**, 459 (1979).
13. P. J. Madec and E. Maréchal, *J. Polym. Sci., Polym. J. Chem. Ed.* **16**, 3157 (1978).