Polymer Bulletin 29, 35–42 (1992)

Polymer Bulletin

Synthesis and characterization of some poly-*p*-silphenylenes

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Summary

The syntheses of some representative low molecular weight poly-p--silphenylenes containing $SiMe_2$ or $SiPh_2$ groups in the main chain are presented. These polymers were obtained from di-Grignard intermediates using either THF or Et_2O as solvent. The insertion of the butylenoxy units in the main chains of the polymers was observed when THF was used as a solvent. The polymers were characterized by a combination of IR, ^1H and ^{13}C - NMR spectra and vapour pressure osmometric analysis. The thermal behaviour of the poly-p-silphenylenes was analysed by thermogravimetry.

Introduction

Polysilphenylenes are very attractive polymers with better thermal stability than polysiloxanes (1) and unusual electronic properties, due to a mixture of σ and π orbitals in the main chain, inducing researches to investigate several potential technological applications (2-5). The polycondensation reaction between di-magnesium derivatives of p-dibromobenzene and dichlorodiorganosilanes is the most useful synthetic route to obtain poly-p-silphenylenes (3). However, the products obtained by this route usually show low values of number average molecular weight and physical aspects varying from white solids to yellowish viscous fluids (1-3). In addition, considerable difficulties have been found in obtaining both high yield and purity in the products obtained from this synthetic procedure (6).

In some reactions involving magnesium in tetrahydrofuran, there is evidence of undesirable by-products (7,8). Yamamoto (9) also described the insertion of $-O(CH_2)_4-$ groups in the main chain of the poly-p-phenylene, coming from the THF ring opening.

The observation of products with a diversity of physical aspects, associated with the possible $-O(CH_2)_4-$ group insertion, and mostly, the rather limited characterization associated with these materials in the literature, stimulated us to synthesize and characterize, as completely as possible in our laboratory, some representative members of this class of compounds.

As such the present paper is concerned with the synthesis, characterization and thermal degradation of some low molecular weight (Mn < 1500) poly-p-silphenylenes. These polymers were obtained from di-Grignard intermediates in THF or Et_2O as a solvent, according to the general reaction scheme:

$$1{,}4C_6H_4X_2 + Mg^o \xrightarrow[\text{reflux}]{\text{solv}} XMgC_6H_4MgX \xrightarrow{R_2SiCl_2} -(SiR_2-C_6H_4)_n-$$

where X = Cl, Br; solv = THF, Et_2O and R = Me, Ph.

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Experimental

All solvents were purified by standard methods, and distilled under argon atmosphere immediately before use. The dichlorosilane monomers obtained from Aldrich were purified by careful distillation. The synthesis procedures were also carried out under an argon atmosphere. 1,4 dibromobenzene, bromobenzene (Carlo Erba) and magnesium fine shavings (Riedel-de-Haën) were used without previous treatment.

Proton and ^{13}C-NMR spectra were recorded on a Varian-Gemini 300 MHz spectrometer, for CCl_4 or $CDCl_3$ polymer solutions. For CCl_4 solutions, D_2O or CH_2Cl_2 were used as reference. The IR spectra were examined in the 4000-400 cm^{-1} region using a Jasco IR-700 spectrophotometer, with samples in KBr pellets or in films over KBr windows. The number average molecular weights ($\bar{M}n$) were determined by vapour pressure osmometry on a Knauer instrument using toluene solutions thermostatically controlled at 45°C. For thermal degradation studies a Du Pont 1090 B thermogravimetric analyser on-line with a Du Pont 951 thermal analyser was used at a heating rate of 10°C/min, under nitrogen atmosphere.

Syntheses

General procedure for Grignard intermediates

A 500 ml three-necked round-bottomed flask, oven-dried and flushed with argon, was fitted with a pressure-equalizing addition funnel, a reflux condenser and an argon inlet. Freshly distilled THF (or Et_2O), 250 ml, and 140 mmol of magnesium fine shavings and iodine crystals were added to the flask which was sonicated with a ultrasonic bath. After that 52 mmol of aryl halide in 30 ml of THF (or Et_2O) were added dropwise at room temperature. After complete addition, the mixture was gently refluxed for 8 h.

General procedure for polymerization reactions

The polycondensation reactions were carried out by adding 50 mmol of diorganodichlorosilane dropwise to the Grignard intermediate, at room temperature. The reaction was kept at reflux for 20 h with vigorous stirring. The growing polymeric chains were blocked by the addition of 40 mmol of PhBr or EtBr, followed by further reflux for 3 h. After this, the solvent and volatile products were removed by distillation. Toluene (100 ml) was added to the resulting solid and the mixture was then hydrolized with 100 ml of 10^{-3} M HCl solution. The organic layer was separated and immediately washed with 100 ml portions of water until neutral pH was attained, and the toluene fraction was dried over sodium sulfate. The solution was concentrated (50 ml) and excess methanol (100 ml) was added, observing in many cases, the precipitation of a white solid. The resulting toluene/methanol mixture was concentrated yielding a yellowish viscous fluid or a resinous solid. The polymer fractions were free of residual solvents at 100°C/3 x 10^{-2} mmHg and were characterized by a combination of IR, ^{1}H and ^{13}C-NMR spectra, vapour pressure osmometric (VPO) and thermogravimetric analyses (TGA).

Results and discussion

It is known that the preparation of poly-p-silphenylenes by di-Grignard intermediates generally produces materials with low values of the number average molecular weight ($\bar{M}n$) and variable physical aspects (1-3,6). The low polycondensation efficiency has been explained by the difficult formation of the Grignard reagent and the limited solubility of this type of polymer, with increasing chain length (10). This is specially true for the $SiPh_2$ derivatives (1).

By the syntheses procedure used in this work, products with low values of $\overline{Mn}$ and variable physical aspects were obtained, as shown in Table 1. In addition, all the products obtained in reactions with THF as solvent, showed insertion of butylenoxy units in the main chain.

Table 1. Reaction conditions, number average molecular weights ($\overline{Mn}$) and physical aspects of the products.

Reaction	Polymer	Aryl Halide	Silane	Solvent	$\overline{Mn}$ (g/mol)	Physical Aspect
1	I*	ClC_6H_4Cl	Me_2SiCl_2	THF	1554	yl
2	II	ClC_6H_4Cl	Me_2SiCl_2	THF	365	yl
3	IIIa	BrC_6H_4Br	Me_2SiCl_2	THF	477	yl
	IIIb				788	wp
4	IVa	BrC_6H_4Br	Me_2SiCl_2	Et_2O	480	yl
	IVb				1400	wp
5	Va	BrC_6H_4Br	Ph_2SiCl_2	THF	634	yr
	Vb				619	wp
6	VIa	BrC_6H_4Br	Ph_2SiCl_2	Et_2O	380	yr
	VIb				340	wp

(*) No blocking agent was used in this reaction; yl = yellowish liquid; yr = yellowish resin; wp = white powder.

The effect of chain blockage on the $\overline{Mn}$ values can be seen by comparing these values for products I and II (Table 1). The hydrolysis of non-blocked chlorosilyl end-groups could promote the condensation of the chains, increasing the $\overline{Mn}$ value of polymer I and the quantity of siloxane groups in the main chain. Evidence for this result can be observed in the infrared spectra of these products, shown in Figure 1. Polymer I presents a broad and intense band in the 1100-1000 cm^{-1} range, which can be assigned to ν SiOSi. In addition, some contribution of ν SiOC might also be observed in this region of the spectrum for the products obtained in THF, due to the presence of butylenoxy units in the main chain (Polymer II).

The examination of Table 1 also shows that products obtained from 1,4 dibromobenzene (DBB) (III) present higher $\overline{Mn}$ values than those from the 1,4 dichlorobenzene (DCB) derivative (II), although the same reaction conditions were used for the synthesis of both. This was expected since DCB is less reactive than DBB, and consequently a larger amount of mono-Grignard derivative, acting as a blocking agent, is formed from DCB.

The polymers with Me_2Si groups in the main chain are very soluble in ether and THF. Analysing products with the same physical aspects and organic substrate origins (syntheses 3 and 4), polymer IVb showed the highest $\overline{Mn}$ value. This suggests a smaller growth of the chains in THF (polymer IIIb) probably due to the insertion of the $-O(CH_2)_4-$ group in the main chain, significantly changing some physical properties, like appearance and solubility. Products of syntheses 5 and 6, which contain $SiPh_2$ in the main chain, are more soluble in THF than in ether, contributing to the greater growth of the chain in the first solvent, in spite of the insertion of $-O(CH_2)_4-$ groups.

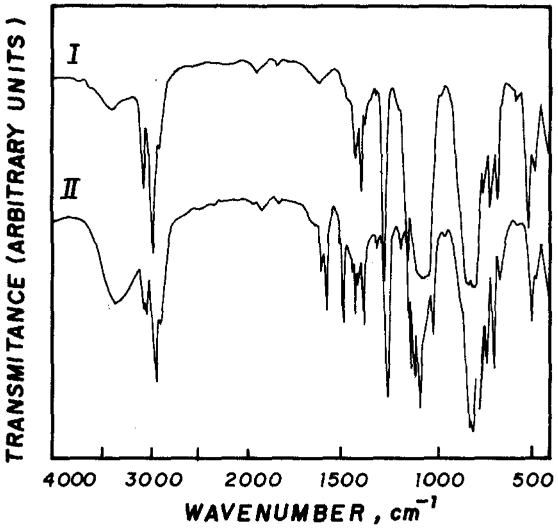

Figure 1. Infrared spectra of I and II polymers. Broad absorptions at 3450 cm^{-1} are due to KBr windows humidity.

Structure caracterization

The infrared spectra of the polymers are in agreement with those expected for polymeric structures containing basically $SiMe_2$ (or $SiPh_2$) and 1,4 C_6H_4 units in the main chain (11,12). In the 1080-1020 cm^{-1} region the presence of the Si-O-Si groups could eventually be observed due to hydrolysis of Si-Cl non-blocked end-groups and also to the presence of Si-O-C groups resulting from $-O(CH_2)_4-$ insertion in the main chain. Assignments for the characteristic IR peaks observed in the products are presented in Table 2.

The polymers show ^1H-NMR spectra with narrow and well-resolved signals, presumably due to low values of $\bar{M}n$ and considerable flexibility in the polymeric backbone, as can be seen in Figure 2A. The aromatic protons of the 1,4 ($Me_2Si-C_6H_4-SiMe_2$) units were observed at $\delta \sim 7.4$ ppm, as a singlet, and as the most intense peak in this spectral range. The protons of the $SiMe_2$ units appeared at $\delta \sim 0.2$ to 0.6 ppm range, as more than one singlet signal, which can be related to the different chemical environments in the main chain.

Figure 3b shows the ^1H-NMR spectrum of one representative polymer with $SiPh_2$ units in the chain. In general these polymers showed peaks in the $\delta \sim 7$-8 ppm range, assigned to aromatic protons of the 1,4 ($Ph_2Si-C_6H_4-SiPh_2$) structure.

The polymers obtained using THF as solvent, show two broad and low intensity peaks at $\delta \sim 1.4$ and 3.6 ppm, attributed to the methylenic protons of the $-O(CH_2)_4-$ groups inserted in the main chain, as can be seen in Figure 2A, product IIIa, and in the Figure 3b (13-15).

Table 2. Characteristic absorptions and peak assignments of the infrared spectra of poly-p-silphenylenes.

Assignment (11,12)	Wavenumber (cm^{-1})
C-H stretching (phenyl)	3040-3060
(CH_3)	2880-2960
(CH_2)*	2930-2860
$-C_6H_4-$, $-C_6H_5$	1585
	1481
	1425
	1378
$SiMe_2$	1250-1260
C_6H_5-Si, $Si-C_6H_4-Si$	1135-1110
Si-O-Si, Si-O-C	1080-1020
$SiMe_2$	815-830
	772
$Si-C_6H_5$, $Si-C_6H_4-Si$	670
$Si-C_6H_5$, $Si-C_6H_4-Si$	740-730
	700-510

(*) $-O(CH_2)_4-$ group.

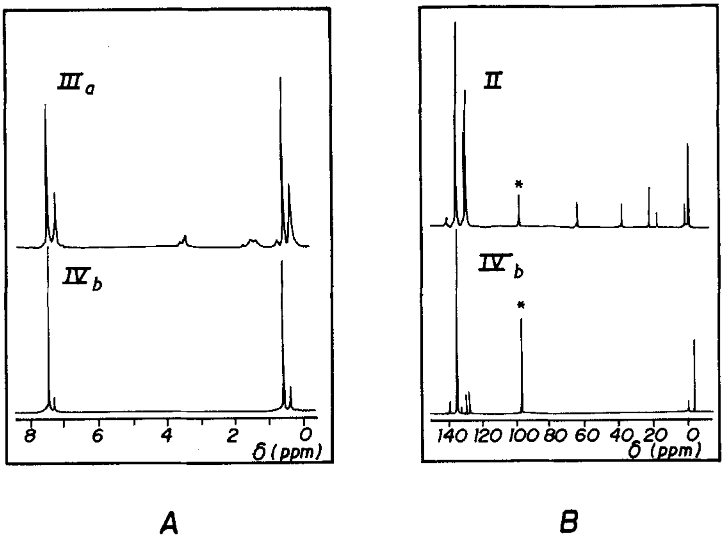

Figure 2. A - ^1H-NMR spectra of IIIa and IVb polymers.
B - ^{13}C-NMR spectra of II and IVb polymers;
(*) CCl_4 peak.

An estimated amount of butylenoxy units inserted in the polymer chains could be calculated from the methylenic protons signals, as is shown in the Table 3. The highest percentage amount of $-O(CH_2)_4-$ group insertion was in product II, obtained from the less reactive 1,4 $C_6H_4Cl_2$ substrate. The insertion was also extensive in the products obtained from the $SiPh_2Cl_2$ monomer. In the reactions with THF as solvent, the white solid products present a smaller amount of $-O(CH_2)_4-$ groups in the main chain, when compared with analogous viscous liquid or resinous products. This fact reinforced the arguments that the butylenoxy units can produce significant physical alterations in the products, due to their higher flexibility which consequently favors the production of less ordered chains.

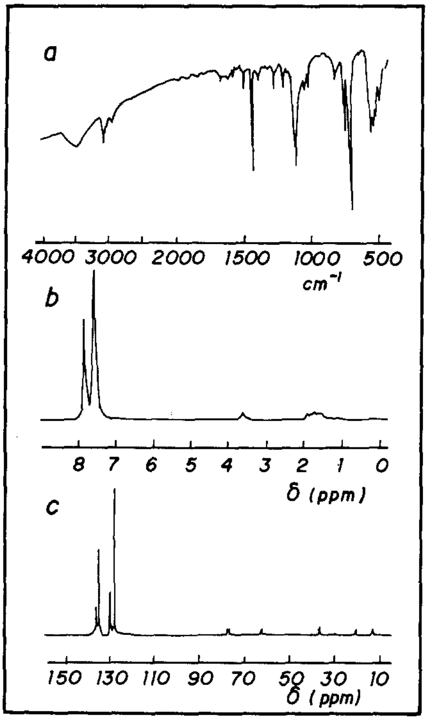

Figure 3. Infrared (a), ^1H-NMR (b), ^{13}C-NMR (c) spectra of Va polymer.

Table 3. % $-O(CH_2)_4-$ groups inserted in the main chain, obtained from ^1H-NMR spectra.

Product	I	II	IIIa	IIIb	Va	Vb
% $-O(CH_2)_4-$*	9.2	19.5	9.6	4.1	16.0	13.1

(*) $-O(CH_2)_4- = I_{mn} \times 100/(I_{mn} + I_{ml} + I_{ar})$, where mn = methylenic protons, ml = methylic protons and ar = aromatic protons.

The insertion of the $-O(CH_2)_4-$ groups in the main chain was also confirmed by ^{13}C-NMR spectroscopy, associated with benzene ring carbon atom chemical shift calculations, using the Ewing (13) and Rakita (14,15) substitution parameters. Figure 2B shows some representative ^{13}C-NMR spectra. It can be seen that the -SiMe$_2$- derivative polymers present the most intense peak at $\delta \sim 134$ ppm, and one of lower intensity at $\delta \sim 138$ ppm, corresponding to carbon atoms 2,3 and 1,4 respectively of the -SiMe$_2$- symmetrically disubstituted ring. The calculated values were 133.4 and 138.7 ppm respectively. The lower $\overline{Mn}$ value polymer II also shows intense signals in the $\delta \sim 127$ to 129 ppm region, related to phenyl ring at the end of the chains, coming from PhBr used as a chain block agent. The sp^3-carbon atoms attached to silicon (SiMe$_2$) resulted in peaks in the $\delta \sim 1$ to -3 ppm region. The -SiPh$_2$- derivative polymers show peaks in the $\delta \sim 134$ to 137 and 127 to 131 ppm regions, which are assigned to carbon atoms of the 1,4 disubstituted rings and of SiPh$_2$ groups respectively (Figure 3c). Four peaks in the $\delta \sim 13$ to 65 ppm region could also be observed in the ^{13}C-NMR spectra of the polymers obtained in THF solvent and were attributed to sp^3-carbon atoms of the -O(CH$_2$)$_4$- groups (15).

Thermal behavior

The thermal stabilities of some representative poly-p-silphenylene samples were studied by thermal gravimetric analysis under nitrogen flow. The results obtained for the polymers are shown in Table 4, where it can be seen that thermal degradation started between 170 to 403°C and ended between 360 to 786°C. Some typical weight - loss curves are shown in Figure 4A.

Phenyl-substituted organosilicon polymers exhibited improved thermal stability. This fact was also observed by Noltes (6) and Yamagushi (1) in poly-p-silphenylenes. However this tendency was not observed in this work, since the TGA curves obtained can not be interpreted directly in terms of the thermal stabilities of the polymers involved. The weight losses and the degradation kinetics during the sample heating are determined by several factors, including the $\overline{Mn}$ values, the volatility of any lower molecular weight constituents of the polymer's sample, the groups sequence in the copolymers and the anomalous units present in the main chain.

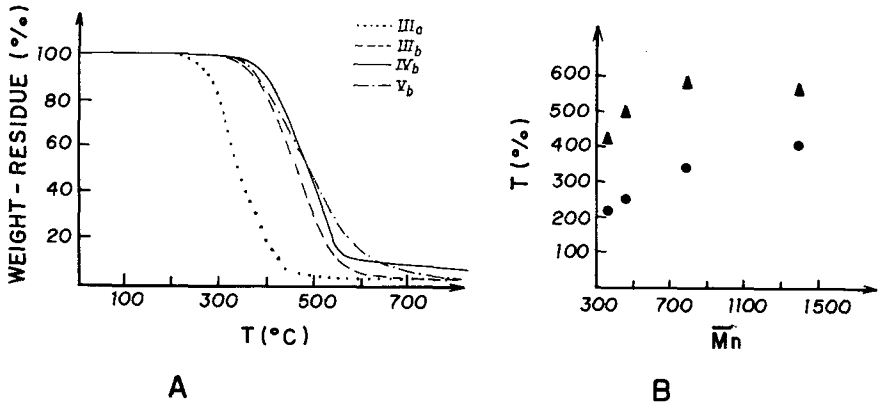

Figure 4. A. Plot of weight-residue against temperature for some poly-p-silphenylenes. B. General tendency related to onset (o) and end (Δ) of degradation of the SiMe$_2$ derivative polymers.

Table 4. Thermal gravimetric analyses of the poly-p-silphenylenes under nitrogen.

Product	Onset of degradation (^{o}C) (T_i)	End of degradation (^{o}C) (T_f)	Weight loss (%)
I	170	600	80
II	220	420	70
IIIa	247	496	98
IIIb	336	579	98
IVa	243	462	97
IVb	403	554	94
Va	178	684	98
Vb	347	786	98
VIa	221	364	93
VIb	223	390	95

Figure 4B showed a general tendency related to the onset and the end of the degradation process of the polymers containing $SiMe_2$ in the chain, with increasing $\overline{M}n$ values. This tendency parallels the decreasing percentage of $-O(CH_2)_4-$ groups inserted in the chain (vide Table 3).

In general, the products obtained as white solids present higher T_i and T_f values than do the yellow liquids or resins obtained in the same reaction. The polymers prepared in this work did not show high conversion to thermally stable products.

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Accepted May 27, 1992 K