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Hydrosilylation of allyl carbonates by polymethylhydrosiloxane and related side-reactions

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ABSTRACT

Hydrosilylation of allyl carbonates by polymethylhydrosiloxane is a rather complex reaction. During the platinum catalyzed modification of polymethylhydrosiloxane with allyl phenyl carbonate, about 50% of the carbonate molecules decompose into CO_2, propene and phenol. The released phenol reacts with the SiH functions of the polymer yielding Si-O-phenyl side groups. However the cleavage reaction can be avoided by using butenyl phenyl carbonate instead of allyl phenyl carbonate.

INTRODUCTION

In a previous paper, we reported the synthesis and properties of liquid crystalline (LC) side-chain polysiloxanes bearing a carbonate group in the spacer (de MARIGNAN et al., 1988). These polymers were prepared by chemical modification of polymethylhydrosiloxane (PMHS) with nematic allyl carbonates obtained by reaction of allyl chloroformate with 4-hydroxyphenyl esters of p-substituted benzoic acid.

Two unsual phenomena were detected in the liquid crystalline properties of the resulting polymers. First, no systematic increase in the order of the mesophases was observed from the nematic allyl precursors to the corresponding modified polymers although the stability of the mesophases was enlarged, as expected. On the other hand, the polymer bearing a terminal cyano group on the side-chain developed a focal conic texture upon annealing, but no typical X-ray diffraction pattern could be obtained and thus the nature of the mesophase could not be established.

A careful reexamination of the NMR spectra of some of these LC polysiloxanes showed that their structure did probably not correspond to the expected one. We thus suspected that some side-reaction leading to a different structure occurred during the hydrosilylation step. In order to identify this side-reaction, we decided to reinvestigate the hydrosilylation of unsaturated carbonates by PMHS, by using a simpler model compound, i.e. allyl phenyl carbonate (APC).

Moreover, our aim was to obtain a polysiloxane bearing $-(CH_2)_x$-O-COO-R side-chains (which is the expected product of the reaction of PMHS with α-unsaturated carbonates) because it would give functional polysiloxanes with ω-hydroxy side-chains through a controlled hydrolysis of the carbonate functions. This method would be simpler than the alternative procedure involving tetrahydropyran intermediates which has been described recently (WU et al.., 1988).

Identification of the side-reaction occurring during hydrosilylation of allyl carbonates as well as the detailed structure of the modified polymers are reported in the present paper. Moreover, a way to avoid this side-reaction and to perform a clean hydrosilylation of unsaturated carbonates is proposed.

EXPERIMENTAL

Synthesis of carbonates

Allyl, ethyl and phenyl chloroformates (Aldrich) were used as received. They were reacted with phenol, ethanol, 1-butanol or 3-butene-1-ol (Aldrich) under phase transfer catalysis conditions, according to a procedure already described (BOIVIN et al., 1983, de

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MARIGNAN et al., 1988). Typically, a solution of chloroformate (0.2 mol) in CH_2Cl_2 (80 ml) was added dropwise to a mixture of the hydroxy compound (0.2 mol), tetrabutylammonium hydrogen sulfate (4 mmol) in CH_2Cl_2 (100 ml), and aqueous 50% NaOH (8 ml). The addition was carried out under nitrogen sufficiently slowly to maintain the temperature below -10°C. At the end of the reaction, the mixture was washed several times with water, and the product was recovered by distillation under vacuum with a yield comprised between 70 and 90%. The purity of allyl phenyl carbonate (APC), allyl ethyl carbonate (AEC), allyl butyl carbonate (ABC), ethyl phenyl carbonate (EPC), and butenyl phenyl carbonate (BPC) was checked by elemental analysis and by ^1H and ^{13}C NMR.

Preparation of side-chain polysiloxanes

PMHS (Merck, DPn=35) was used as received. In a typical experiment, allyl carbonate (20.0 mmol) in dry toluene (20 ml) was stirred with PMHS (16.7 meq. of SiH) at 60°C under nitrogen, in the presence of platinum cyclovinylmethylsiloxane complex (PCO 85, Petrarch Systems, 1.7 10^{-4} mmol). The reaction was followed by monitoring the decrease of the SiH IR band at 2165 cm^{-1} and/or of the ^1H resonance at 4.8 ppm of the SiH. The polymer was recovered by precipitations in hexane and purified by several dissolutions in methylene chloride and precipitations in hexane. The product was then dried under high vacuum.

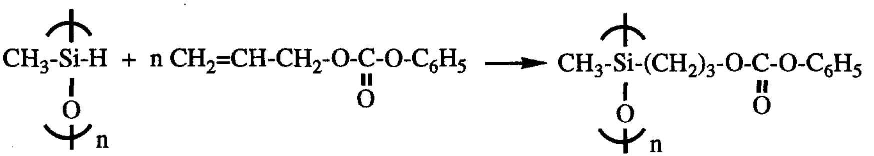
Physicochemical characterizations

IR spectra were recorded on a Perkin-Elmer 577 apparatus. The ^1H, ^{13}C and ^{29}Si NMR spectra were recorded at 200, 50.3 and 40 MHz, respectively, in $CDCl_3$ at 25°C,with a AM 200 SY Bruker apparatus.

RESULTS AND DISCUSSION

Hydrosilylation of allyl phenyl carbonate by PMHS

The chemical modification of PMHS with APC should normally correspond to the following equation if hydrosilylation of the allyl carbonate proceeds without side reaction :



$$\left(\mathrm{CH_3{-}\underset{\underset{O}{|}}{Si}{-}H}\right)_n + n\,\mathrm{CH_2{=}CH{-}CH_2{-}O{-}\underset{\underset{O}{\|}}{C}{-}O{-}C_6H_5} \longrightarrow \left(\mathrm{CH_3{-}\underset{\underset{O}{|}}{Si}{-}(CH_2)_3{-}O{-}\underset{\underset{O}{\|}}{C}{-}O{-}C_6H_5}\right)_n \quad (1)$$

However, the ^1H NMR spectrum of the modified polymer shows some discrepancies with the expected formula (Fig. 1). The signal corresponding to the protons of the methyl group bound to the silicon atom exhibits a clear splitting into two peaks at 0.11 and 0.23 ppm. This suggests the occurrence ot two types of silicon atoms in the backbone, i.e. silicon atoms bearing side-groups of different nature. This is confirmed by the presence of two signals corresponding to the methyl carbons bound to the Si atom at -0,9 and -3.9 ppm in the ^{13}C NMR spectrum. Moreover, the relative integrations in the ^1H NMR spectrum of the modified polymer do not correspond to the expected formula. The ratio of the aromatic protons (from the phenyl ring) to the aliphatic protons of the spacer $-(CH_2)_3-$ is too large by a factor of ca.2.. The same excess appears in the ratio of the methyl protons bound to the Si atoms compared to the aliphatic protons of the spacer. In addition, two small extra signals at 0.6 and 0.9 ppm suggest the occurrence of a small proportion of α-(Markovnikov) addition of the unsaturated carbonate.

^{29}Si NMR of polysiloxanes allows a clear distinction between the Si atoms of the backbone according to the number of oxygen atoms surrounding each Si atom (GRAY et al., 1989). In the ^{29}Si NMR spectrum of the modified polymer (Fig. 2), the terminal trimethyl siloxy units appear at around 10 ppm whereas the methyl siloxy units substituted in the expected way by APC appear at around -21 ppm. However, an important signal located at -62 ppm indicates that the polymer contains a certain proportion of Si atoms surrounded by three oxygen atoms which cannot come from a normal hydrosilylation of

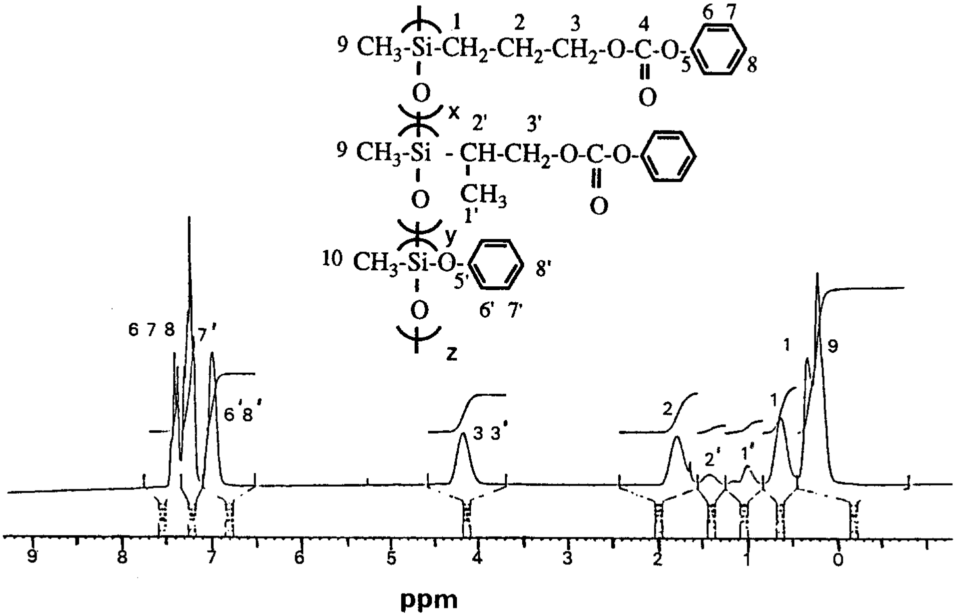


Fig.1 ^{1}H NMR spectrum (200 MHz) of PMHS modified with allyl phenyl carbonate in $CDCl_3$ at 25°C

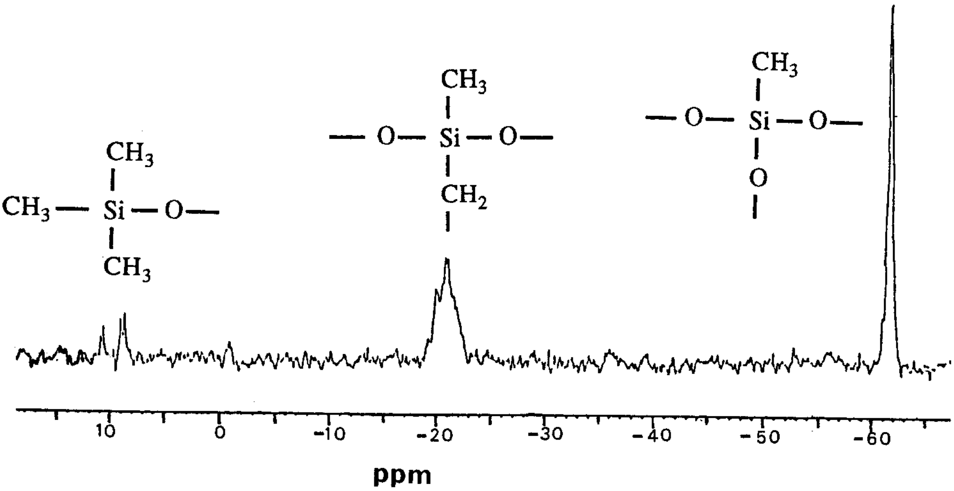
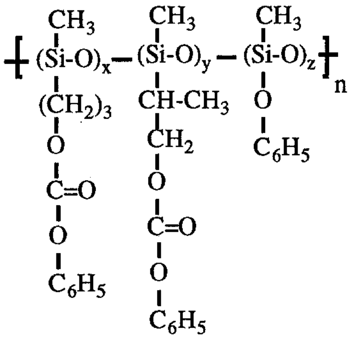


Fig.2 ^{29}Si NMR spectrum (40 MHz) of PMHS modified with allyl phenyl carbonate in $CDCl_3$ at 25°C the unsaturated carbonate. Several experimental proofs which will be developed in the following section show that this signal at -62 ppm indicates corresponds to Si atoms substituted by phenoxy groups which results from the cleavage of allyl phenyl carbonate.

Cleavage of unsaturated carbonates under hydrosilylation conditions

TLC analysis of several aliquots of the reaction mixture during the hydrosilylation of APC by PMHS, shows that a certain amount of phenol is released. Moreover, the evolution of gas is observed at the beginning of the reaction, which have been identified as propene (by GC analysis) and CO_2 (by bubbling into a saturated solution of calcium hydroxide which produces a $CaCO_3$ precipitate). Thus it appears that during the course of the hydrosilylation, a certain proportion of APC molecules is cleaved into CO_2, propene and phenol. The released phenol would then easily react with SiH groups on the polymer, and this would account for the presence of phenoxy side-groups in the final product. This point is confirmed by the presence of two types of carbon atoms corresponding to two types of phenyl groups in the ^{13}C NMR spectrum of the modified polymer.

The structure of the final product is thus quite different from the expected one proposed in Eq. (1). The following structure is in better agreement with the experimental data reported here :



$$\left[(\overset{CH_3}{\underset{(CH_2)_3-O-C(=O)-O-C_6H_5}{Si}}\text{-}O)_x-(\overset{CH_3}{\underset{CH(CH_3)-CH_2-O-C(=O)-O-C_6H_5}{Si}}\text{-}O)_y-(\overset{CH_3}{\underset{O-C_6H_5}{Si}}\text{-}O)_z\right]_n \qquad (2)$$

x=0.4
y=0.1
z=0.5

Several blank experiments as well as reactions with other model compounds have been carried out in order to investigate the reasons for the cleavage of APC during the hydrosilylation by PMHS. The results collected in Table 1 show that the simultaneous presence of the SiH groups, the Pt catalyst and the allyl group on the carbonate (but not a phenyl group) is essential to promote the cleavage of the carbonate molecule.

Although it is a slightly different case, the cleavage of an ester function during a hydrosilylation reaction has been reported several years ago (LIN and NAKOS, 1985). It has been observed that the hydrosilylation of methacrylate esters by PMHS consistently leads to a 30% grafting through a Si-O-C hydrolyzable bond together with the elimination of propane.

On the other hand, the formation of carbonate esters, and particularly the allyloxycarbonyl group (STEVENS and WATANABE, 1950) is often used for the protection of amine or alcohol functions. Among the deprotection procedures leading to the regeneration of the initial alcohol, $Ni(CO)_4$ can promote the cleavage of the allyloxycarbonyl group (COREY and SUGGS, 1973). More recently, a highly selective and mild deprotection method involving a palladium catalyzed hydrostannolysis by Bu_3SnH has been proposed (GUIBE and SAINT M'LEUX, 1981, GUIBE et al., 1986). Thus, it seems reasonable to assume that the -SiH/Pt catalyst system could act in the same way as the -SnH/Pd catalyst system and promote the cleavage of the allyl carbonates during their hydrosilylation.

In order to check this assumption, hydrosilylation by PMHS of an unsaturated carbonate in which the terminal vinyl group is further apart from the carbonate function, i.e. butenyl phenyl carbonate, has been examined. The reaction proceeds almost without any cleavage, and only 4% of phenoxy adducts appear in the modified polymer as shown by ^{1}H and ^{29}Si NMR.

Thus the presence of two types of mesogenic side-chains - one "normal" and the other without alkoxycarbonyl spacer - in the LC polysiloxanes reported previoulsy (de MARIGNAN et al., 1988) could explain why well-defined LC structures could not be identified. The synthesis of new LC side-chain polysiloxanes modified by butenyl carbonyl mesogenic groups is in progress.

Table 1. Hydrosilylation of carbonates [a)]

Run	Reagents	Cleavage of carbonates (%) [b)]
1	APC+PMHS $\xrightarrow{\text{with Pt Cat.}}$	50
2	APC+PMHS $\xrightarrow{\text{without Pt Cat.}}$	No
3	APC+Pt cat. $\xrightarrow{\text{without PMHS}}$ 1 : 10^{-4} (molar ratio)	No
4	APC+Pt cat. $\xrightarrow{\text{without PMHS}}$ 1 : 5×10^{-3} (molar ratio)	5
5	ABC+PMHS $\xrightarrow{\text{with Pt Cat.}}$	50
6	AEC+PMHS $\xrightarrow{\text{with Pt Cat.}}$	50
7	EPC+PMHS $\xrightarrow{\text{with Pt Cat.}}$	No

[a)] carried out under N_2, at 60°C, in dry toluene (t=16 h). the molar ratios between the reagents are identical to those reported in the experimental section except for runs 2 and 3. APC = allyl phenyl carbonate; ABC : allyl butyl carbonate; AEC : allyl ethyl carbonate; EPC : ethyl phenyl carbonate. [b)] determined by ^{1}H NMR from the ratio of the phenyl protons to the methyl protons bound to the silicon atom in the resulting purified polymers; also checked by TLC.

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