

Synthesis of Statistical Polydiene Networks by Reaction of Liquid Polyenes with Telechelic Siloxanes

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Abstract

The present investigation concerns the synthesis of statistical networks similar to vulcanized rubber. We have used liquid precursor polymers: polybutadiene (PB) and polyisoprene (PI) with telechelic siloxanes. The reactivity of the polydienes can be classified as follows : PB units 1,2 >>> PI units 3,4 >>> PI units 1,4 \approx 0. The network formation is a function of the ratio $R = \text{nb. of pendent double bonds/nb. of } \text{>SiH}$. For $R \approx 1$ the networks are rather hard and brittle, for $8 \leq R \leq 10$ they are soft and elastic, whereas for $R \approx 16$ the gels obtained are very soft and sticky.

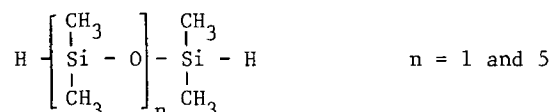
INTRODUCTION

Crosslinked rubbers are usually prepared by one of the numerous classical vulcanization methods leading to bridges between linear precursor chains. More recently much interest has been devoted to the synthesis of rubber networks based on the reaction of short liquid telechelic polymer chains with plurifunctional crosslinkers.

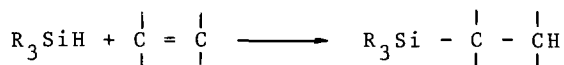
The aim of the present investigation was to synthesize statistical networks similar to vulcanized rubber, i.e. networks with a statistical distribution of the crosslinks and of the lengths of the elastic chains, and to study their macroscopic behaviour in relation with their chemical structure.

For this purpose we have used liquid precursor polymers such as low molecular weight polyisoprenes and polybutadienes containing a large proportion of pendent double bonds capable to react with a difunctional antagonist compound.

As crosslinker we have chosen small telechelic polysiloxanes fitted at both ends with hydrogenosilane functions:



It is well-known that R_3SiH reacts with a double bond according to the following scheme :



This addition reaction (hydrosilylation reaction), which has already been described by Sommers (1) and more recently by Speier (2,3) takes place in the presence of catalysts of various types such as peroxides (1), platinum derivatives (4), azoic compounds (5). Later on a large number of synthesis based on this reaction has been reported in the literature. A quite extensive investigation in this field has been published by Greber (6). The hydrosilylation reaction has also been applied to the preparation of block copolymers (7,8) and to the synthesis of polydimethylsiloxane model-networks used in rubber-elasticity studies (9-13).

In the present investigation we have chosen this reaction to achieve crosslinking of polydienes by means of α - ω dihydrogensiloxane oligomers of molecular weight smaller than 500. These compounds are liquid at room temperature and can be mixed easily with liquid polydienes to yield homogeneous transparent blends.

We have studied the network formation as a function of the molecular weight of the crosslinking agent and of the polydienes, of the catalyst concentration and of the ratio :

$$R = \frac{\text{nb. of pendent double bonds}}{\text{nb. of } \begin{array}{c} \text{>} \\ \text{SiH} \end{array}}$$

In order to compare the efficiency of the crosslinking reaction in these experiments we have characterized the networks obtained by their equilibrium swelling degree Q .

EXPERIMENTAL

. Synthesis of prepolymers - Low molecular weight polyisoprenes were prepared in THF at 20°C by the classical anionic polymerization procedure, in a glass reactor under argon atmosphere. The initiator used was lithium-naphthalene. Monomer and solvent were purified according to the usual methods. Polyisoprenes with average molecular weights $\bar{M}_n = 1500$ and 4000 thus prepared, contained 63% units 3,4, \bar{M}_n 18% units 1,2 and 19% units 1,4 cis. Polybutadienes of average molecular weight $\bar{M}_n = 1500$ were prepared in the same way, in THF, but at -50°C. Their microstructure was the following: 84% of units 1,2 and 16% units 1,4.

The siloxane oligomer with $n = 5$, dihydrogeno-1,11-dodecamethyl-1,1,3,3,5,5,7,7,9,9,11,11 hexasiloxane ($M'D_4M'$), has been prepared by reacting octamethylcyclotetrasiloxane with dihydrogeno-1,3 tetramethyl-2,2,3,3 disiloxane (14).

. Synthesis of networks - The crosslinking reaction is carried out at 20°C and 70°C in the bulk after careful mixing of the oligomeric reagents and in the presence of chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$). The experimental conditions are gathered on table 1. These networks contain a fraction of soluble polymer which has to be extracted with benzene.

. Swelling measurements - The crosslinked samples, free of soluble polymer, have been characterized by their swelling behaviour. Their equilibrium swelling degrees Q have been measured in benzene. To determine Q we have used the weighing procedure described by Weiss and al. (15). The volume swelling degree is given by the relationship $Q = 1 + (G-1) \frac{V_s}{V_p}$ where G represents the swelling degree by weight. V_s and V_p are the specific volumes of the solvent and of the crosslinked polymer. We have assumed in a first approximation that V_p for the network is the same as for the corresponding linear polymer.

RESULTS AND DISCUSSION

The principal results obtained from our experiments have been summarized in Table 1.

These experiments show that network formation occurs only when polyisoprene (PI) and polybutadiene (PB) with pendent double bonds are used as precursor material.

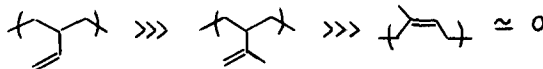
All our attempts to prepare networks with a polyisoprene 1,4 cis precursor failed (under the experimental conditions mentioned on Table 1).

On the other hand, the time τ required to reach the gel point (Table 1), which is characterized by a sudden increase of the viscosity of the reaction media and followed immediately by gelification of the latter, appears to be appreciably longer for PI than for PB under comparable experimental conditions.

Moreover in the case of PI, network formation is possible only at temperatures close to 70°C whereas for PB crosslinking is still possible even at 20°C, although the reaction time τ is much longer: for $R = 1$, $\tau = 20$ mn at 70°C and $\tau = 30$ h at 20°C.

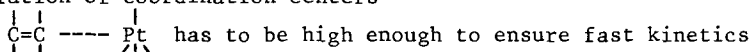
The steric effect due to the methyl group at the double bond is an important parameter. Thus, in the case of PI 1,4 no crosslinking occurs. For PI 3,4 (exp. N° 6, Table 1) the time interval between the start of the reaction and the gel point is clearly larger than for PB 1,2 (exp. N° 8) under identical experimental conditions.

The reactivity corresponding to these three structures can be classified as follows :



The catalyst concentration has an influence on the rate of the network formation, on the proportion of extractable polymer and on the equilibrium swelling degree of the network obtained.

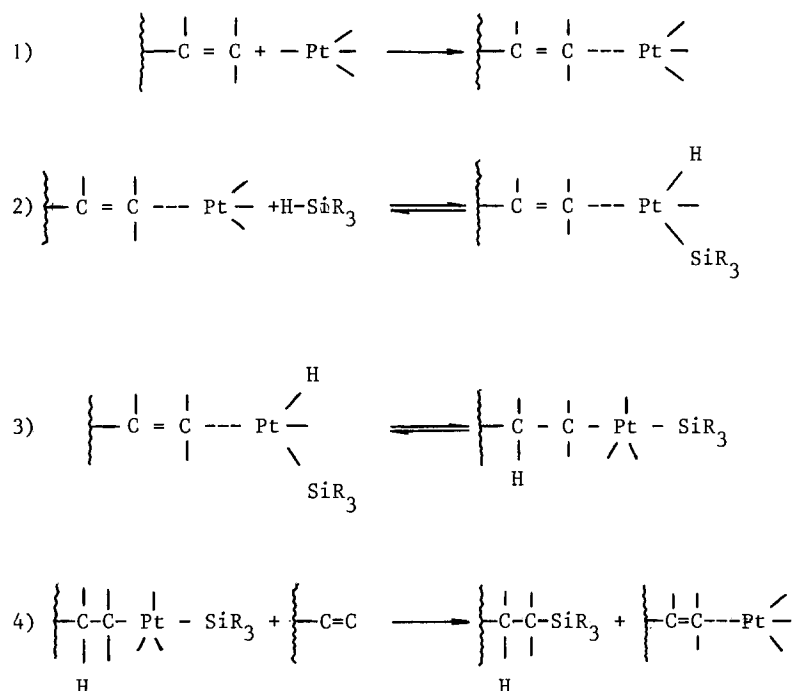
Considering the mechanism of the hydrosilylation reaction proposed by Chalk (16,17) shown on scheme 1, and taking into account the experimental results obtained, we can conclude that the concentration of coordination centers



| N° | \bar{M}_n (PI) | M'D ₄ M' | R | R ₁ | R ₂ | t °C | Q | τ (h) | P _E | Observations |
|---|---------------------|---------------------|----|-------------------|--------------------|------|------|---------------|----------------|--------------|
| 6 | 1500 | M'D ₄ M' | 1 | 10 ⁵ | 10 ⁵ | 70 | 7,7 | 72 | 21 | soft → hard |
| 14 | " | M' ₂ | 16 | " | 16.10 ⁵ | 70 | - | - | - | no |
| 1 | " | M' ₂ | 1 | " | 10 ⁵ | 20 | - | - | - | crosslinking |
| 2 | " | M'D ₄ M' | 1 | " | 10 ⁵ | 20 | - | - | - | " |
| ===== | | | | | | | | | | |
| 5 | 4000 | M'D ₄ M' | 1 | " | 10 ⁵ | 70 | 1,6 | 1 | 7 | hard |
| 7 | " | " | 2 | " | 2.10 ⁵ | " | 2,1 | 4 | 4 | soft → hard |
| 10 | " | " | 10 | " | 10.10 ⁵ | " | 12,3 | 96 | 10 | hard |
| 13 | " | M' ₂ | 16 | " | 16.10 ⁵ | " | - | - | - | no |
| 14 | " | M'D ₄ M' | 16 | " | " | " | - | - | - | crosslinking |
| 3 | " | " | 1 | " | 10 ⁵ | 20 | - | - | - | " |
| ===== | | | | | | | | | | |
| (PB) | | | | | | | | | | |
| 1 | 1500 | M'D ₄ M' | 4 | 10 ⁵ | 4.10 ⁵ | 70 | 8,1 | 7 | 23 | soft → hard |
| 6 | " | " | 16 | " | 16.10 ⁵ | " | 27 | 72 | 32 | sticky |
| 8 | " | M' ₂ | 1 | " | 10 ⁵ | " | 1,5 | 0,5 | 0 | hard |
| 2 | " | " | 4 | " | 4.10 ⁵ | " | 5 | 4 | 15 | soft → hard |
| 3 | " | " | 8 | " | 8.10 ⁵ | " | 5,3 | 20 | 17 | elastic |
| 5 | " | " | 16 | " | 16.10 ⁵ | " | 31 | 144 | 46 | sticky |
| 10 | " | " | 16 | 6.10 ³ | 10 ⁵ | " | 15,8 | 2 | 25 | soft |
| 9 | " | " | 1 | 10 ⁵ | 10 ⁵ | 20 | 1,7 | 29 | 0 | hard |
| 4 | " | " | 4 | " | 4.10 ⁵ | " | 2,8 | 192 | 6 | soft → hard |
| ----- | | | | | | | | | | |
| M' ₂ : H-Si(CH ₃) ₂ -O-Si(CH ₃) ₂ -H | | | | | | | | | | |
| M'D ₄ M' .. : H- Si(CH ₃) ₂ -O ₅ -Si(CH ₃) ₂ -H | | | | | | | | | | |
| R ₂ : C=C/Pt, R ₁ : SiH/Pt, R : C=C/SiH | | | | | | | | | | |
| t °C : temperature at which the networks were prepared | | | | | | | | | | |
| Q : equilibrium swelling degree in benzene | | | | | | | | | | |
| τ : time required to reach the gel point | | | | | | | | | | |
| P _E : % by weight of extractable polymer | | | | | | | | | | |

Table 1 - Synthesis and characterization of polyene-siloxane networks

and to reduce the influence of possible side reactions. In this case the amount of extractable polymer is low. The ratio C=C/Pt is of particular importance at the proximity of the gel point when the viscosity of the reaction media increases very rapidly: crosslinking may hinder considerably or even block step 4 shown on scheme 1.



Scheme 1

Therefore it is necessary that at the gel point the optimal number of antagonist molecules is built in the network (PB N° 5 and 10, Table 1). Side reactions between polydiene and chloroplatinic acid are of noticeable importance only in the case PI, at least within the range of catalyst concentrations used in these experiments. The soluble polymer extracted from the gels has been examined by proton NMR. The NMR spectra obtained is characteristic for a cyclic polyisoprene 3,4 (Fig. 1).

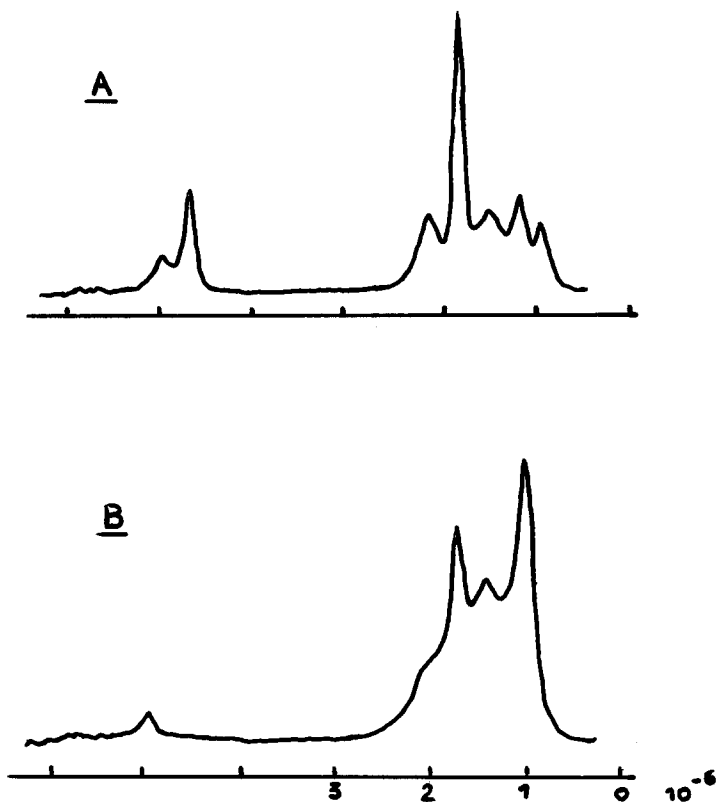


Fig. 1 - NMR spectra of 3,4-polyisoprene sample before (A) and after crosslinking and extraction (B)

The first signal corresponding to the olefinic protons at 4.6×10^{-6} ($C=CH_2$: 3,4 addition) disappears completely, the intensity of the second one at 4.95×10^{-6} ($CH=$ 1,4 addition and $C=CH_2$: 3,4 addition) decreases, whereas three strong signals appear at 0.95×10^{-6} (CH_3-C), 1.25×10^{-6} (CH_2-C) and 1.6×10^{-6} ($CH_3-C=$), which correspond to the protons of the cyclic structure (18).

The NMR spectrum of the extractable PB is the same as that of the precursor polymer: we do not observe any cyclization in this case. Still another parameter which influences the crosslinking reaction seems to be the ratio $C=C/Pt$. It has to be chosen in a way to ensure fast crosslinking.

The equilibrium swelling degree Q of the networks increases with increasing values of the ratio R .

Q fluctuates in a large domain (1.5 to 30) and depends upon R , the respective molecular weights of the precursor polymers and of the crosslinking agent.

For $R \approx 1$, the networks are rather hard and brittle, for $8 \leq R \leq 10$ they are soft and elastic, whereas for $R \approx 16$ the gels obtained are very soft and sticky.

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Received December 2, accepted December 8, 1981