2. Synthesis of Statistical Networks
from Liquid Telechelic Dimethylhydrogenosilane Polydiene

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Abstract
A new route to the synthesis of statistical networks similar
to vulcanized rubber, from 1,2-polybutadiene (PBD) and 3,4-poly-
isoprene (PI) is described. The two antagonist chemical
functions are both present on the polydiene backbone. The latter
could be used as precursor polymer and as difunctional cross-
linker simultaneously; the reactive groups are respectively
the dimethylhydrogenosilane end groups and the pendent double
bonds along the Polydiene backbone.

INTRODUCTION
In the present work we tested a new route to the synthesis of
statistical networks. The liquid polymer precursor (PBD) or (PI)
is functionalized with hydrogenosilane groups at both ends.
The one step crosslinking reaction is carried out in the bulk
after mixing the functionalized polydienes with the catalyst.

EXPERIMENTAL
1,2-polybutadiene and 3,4-polyisoprene: dilithium adducts there
off. Their synthesis is already described elsewhere (G.Friedmann,
1982). The microstructure were respectively the following :84%
units 1,2 and 16% units 1,4 for (PBD), 63% units 3,4, 18% units
1,2 and 19% units 1,4 cis for PI.

Functionalization with dimethylchlorosilane (DMCS)
A solution of polybutadienyl-dilithium (or polyisoprenyl-di-
lithium (0.05 equivalent Li) in 300 ml THF was stirred at - 70°C
in a dry flask under nitrogen (G.Greber et al. 1963). Then a solu-
tion of DMCS (0.06 moles) in 200 ml THF was added dropwise
over a period of 30 minutes. This addition was followed by an
additional 2 h of stirring at - 70°C. The functionalized PBD or
PI solution was then concentrated under vacuum and the resul-
ting solution was poured into 500 ml of methanol. The liquid
polymer was isolated, dissolved in benzene, precipitated in
methanol and dried at 40°C under vacuum (IR spectrum: 2100 cm
-1

Purification of DMCS
The commercial product (Aldrich) was kept over molecular sieves
4 Å and distilled just before use, under nitrogen.
Synthesis of networks

The crosslinking reaction is carried out at 80°C, in the bulk after careful mixing of the functionalized polymer with the catalyst.

Catalyst

The platinum catalyst (Prolabo) is a solution of hexachloroplatinic acid in isopropylalcohol (2.07 x 10^{-2} mole.l^{-1}).

Swelling measurements


RESULTS AND DISCUSSION

Liquid α,ω-dilithiated 1,2-PBD or 3,4-PI are functionalized with dimethylhydrogenosilane groups according to scheme 1 and crosslinked by mixing with H₂PtCl₆·6H₂O at 80°C; the latter reaction is based on the classical addition reaction of a hydrosilane onto a vinyl double bond according to scheme 2:

\[ \text{Si-H + CH}_2=\text{CH} \xrightarrow{\text{Pt}} \text{Si-CH}_2-\text{CH}_2 \]

The feasibility of this type of reaction for the preparation of statistical networks has been tested. The reaction involved is a one step reaction in which the crosslinks give rise to a statistical distribution and the functionality of the liquid precursor polymer (if we consider the number of end groups) could be slightly different from two without interfering the network synthesis. The influence of the usual defects, such as loops, trapped entanglements or pendant double chains (chains linked by one chain end only to the network) on the physical properties is no more significant. If loops are formed they are still engaged in the structure of the networks by means of their remaining pendant double bonds. Therefore they could be considered as a mesh of the networks.

The rate of the crosslink reaction depends on the ratio \( R = \frac{\text{nb pendant double bonds}}{\text{nb Si-H}} \) (G. Friedmann, 1982) and less on the catalyst concentration. In the present synthesis, \( R = 15 \), is directly governed by the molecular weight of the liquid precursor polymer. The experimental results when "auto-crosslinking" H-Si-PBD-Si-H, are summarized in table 1 (\( M_n \) (PBD) = 1600).