Polymer Bulletin 11, 25–27 (1984)

Polymer Bulletin

3. Telechelic Diene Prepolymers:

Oligomers of Butadiene with Hydrogenosilane Endgroups

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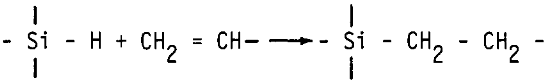
ABSTRACT

A one step synthesis of butadiene telechelic prepolymer is reported here. Butadiene is reacted with metallic lithium in tetrahydrofurane in the presence of dimethylchlorosilane. This typical synthesis leads to α,ω-dihydrogenodisilane dimers, trimers and tetramers of butadiene, which can be used as crosslinkers for the synthesis of rubber like networks. These oligomers have been characterized by usual methods such as ^{1}H.NMR, IR spectroscopy, gel permeation and gas chromatography.

INTRODUCTION

To achieve the synthesis of macromolecular networks from a liquid precursor polymer, in absence of solvent, it is necessary to have a good compatibility between the polymer and the crosslinking agent. The possibility to obtain a homogeneous solution depends upon the solubility parameters of the two reactants. Our approach to this problem is to use a liquid telechelic crosslinker of the same structural family as the liquid precursor polymer. Therefore we have worked out a one step synthesis of a mixture of butadiene dimers, trimers and tetramers fitted at both ends with a hydrogenosilane group.The synthesis of the networks, already described elsewhere (G. FRIEDMANN, 1982) is based on the classical addition reaction of a hydrogenosilane (hydrosilylation) onto a vinyl double bond according to scheme 1, as described by SOMMER and al. (2) and SPEIER and al. (3,4):



$$-\overset{|}{\underset{|}{Si}}-H + CH_2=CH- \longrightarrow -\overset{|}{\underset{|}{Si}}-CH_2-CH_2-$$

scheme 1

EXPERIMENTAL

Synthesis of $HSi(CH_3)_2-[C_4H_6]_n-Si(CH_3)_2H$: n = 2,3 and 4

The reaction is carried out in a 1000 ml flask fitted with a dropping funnel, an argon gas inlet and a condenser. 0.29 mole (2.01 g) of finely dispersed metallic lithium are added to 500 ml of dry. THF, under argon. After cooling to -60°C the lithium suspension is magnetically stirred. 0.06 mole (5 ml) butadiene are then condensed in this mixture which turns inot yellow pale after about 10 mn. Then butadiene (0.42 mole, 40 ml). and dimethylchlorosilane (0.22 mole, 24 ml) are simultaneously introduced so that the yellow colour of the mixture remains still the end of the addition.

After 5 h. at -60°C the mixture is slowly heated to ambiant temperature and deactivated with 5 ml methanol. THF is then eliminated by distillation. The residue is purified by dissolving in 100 ml benzene, filtered off and benzene is removed by distillation under reduced pressure. This purifying process is repeated three times. A colourless liquid is obtained (20.5g) consisting of a mixture of telechelic dimer, trimer and tetramer of butadiene.

T_E (2 mm) = 121°C, M_n (tonometry) = 295

The yield of the reaction is 44% by weight versus the initial quantities of butadiene and dimethylchlorosilane.

RESULTS AND DISCUSSION

The oligomeric mixture has been characterized by its ^{1}H.NMR spectrum (fig.1), by gas chromatography (fig.2), IR spectrometry, gel permeation liquid chromatography and tonometry.

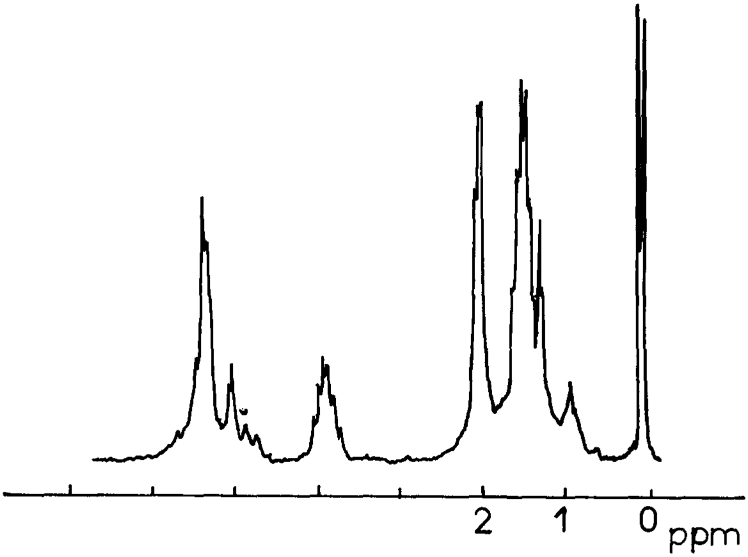


Fig.1 - ^{1}H.NMR spectrum of the telechelic butadiene oligomers

This typical synthesis gives rise to 77% 1.4 oligomers of butadiene and 23% 1.2 structural units. The assignement of the different peaks is the following (reference: TMS, solvent: CCl_4), 0.2 ppm: $Si(CH_3)_2$ (1.2 and 1.4. structural units); 0.9 ppm: $Si-CH_2$ (1.2 units); 1.25 ppm: $CH_2 - C$ (1.2 units); 1.45 ppm: $Si - CH_2 - C = C$ and $Si - CH - C = C$ (1.4 and 1.2 units); 3.80 ppm: $Si - H$ (1.4 and 1.2 units); 4.75 ppm: $CH_2 = C - C$ (1.2 units); 5.30 ppm: $CH = CH$ and $CH = C$ (1.4 and 1.2 units).

The IR spectrum shows a sharp peak at 2 100 cm^{-1} due to the Si-H valence vibration. The gas chromatogram of the products obtained shows three main peaks (N° 2,3 and 4 in fig.2) present in the following proportions: 33% 47% and 20%. We assume that they correspond respectively to the dimer, trimer and tetramer so that one can calculate for the mixture the following molecular weight average: M_n : 271, $M_w = 276$ and $M_z = 281$. This assumption is confirmed by the molecular weight determination by gel permeation using the universal calibration method (Z. GRUBISIC and al. 1967): $M_n = 216$, $M_w = 276$ and $M_z = 295$. M_n measured by tonometry in benzene is 295.

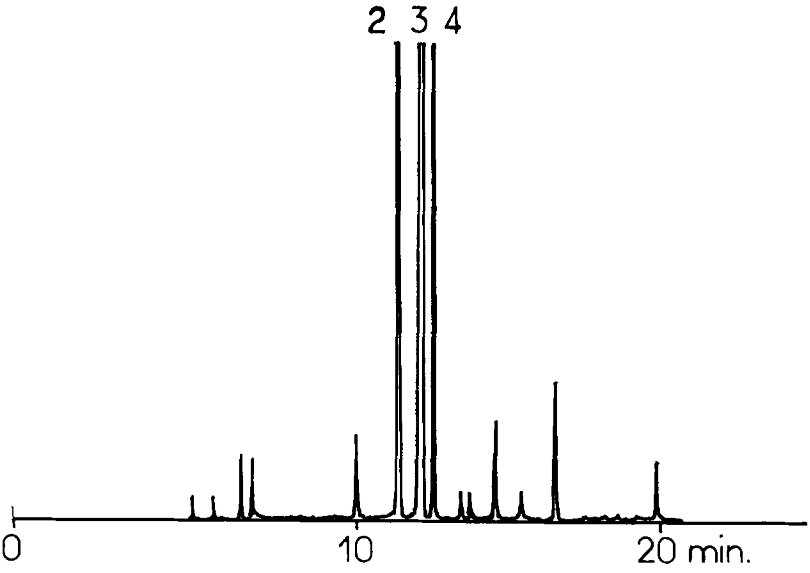


Fig.2 - Gas chromatography of the telechelic butadiene oligomers (stationary phase: Dexsil 300, 3% chromosorb 100/120; column: 3 m; injector temperature: 210°C; column: 60°C - 220°C; temperature programme: 10°C $min.^{-1}$, 2 min. at 60°C, 6 min. at 220°C)

These telechelic oligomers of butadiene have been used as potential cross linkers for the synthesis of rubberlike networks, in the presence of liquid precursor polymers fitted with pendent double bonds along the chain. The method of crosslinking has been described in a previous publication (G. FRIEDMANN, 1982).

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Accepted October 2, 1983