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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-polyisoprene (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 polybutadienyldilithium (or polyisoprenyl-dilithium (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 solution of DMCS (0.06 moles) in 200 ml THF was added dropwise ower 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 resulting 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} Si-H stretching) (L.J. Bellamy, 1958).

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 carefull mixing of the functionalized polymer with the catalyst.

Catalyst

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

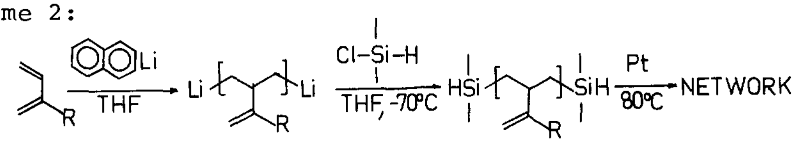
Swelling measurements

The process is already described elsewhere (G.Friedmann, 1982, P. Weiss et al. 1970).

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 $H_2PtCl_6, 6\ H_2O$ 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:

(1)



(2) $$\sim\!\!\sim\overset{|}{\underset{|}{Si}} - H + CH_2 = CH -\big\} \xrightarrow{Pt} \sim\!\!\sim\overset{|}{\underset{|}{Si}} - CH_2 - CH_2 -\big\}$$

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 pendent 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 pendent double bonds. Therefore they could be considered as a mesh of the networks.

The rate of the crosslink reaction depends on the ratio R=nb pendent double bonds/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($\bar{M}_n$ (PBD) = 1600).

Table 1

N°	T°C	H_2PtCl_6 (mole)	R	R_p	Q	P_E (%)	τ (mm)
1	80	5.10^{-7}	15	$1{,}2 \times 10^4$	5.6	2	45
2^x	80	"	"	"	6.4	3-4	30

Q : equilibrium swelling degree in benzene, R : nb pendent double bonds/ nb Si-H, R_p : polymer /H_2PtCl_6, 6 H_2O (by weight), P_E : % by weight of extractable polymer, τ : time required to reach the gel point, 2^x : the network was obtained as a film.

We can observe, though R would be high, that crosslinking proceeds rapidly. The time required to reach the gel point is 30 mn in the case of the network obtained as a film of 1 mm thickness.

CONCLUSION

The value of the equilibrium swelling degree in benzene and the extractable polymer significantly decrease if compared with the results obtained in our previous work (G. Friedmann, 1982) . These data confirm that the hydrosilylation reaction can be applied successfully to the synthesis of statistical networks, using as precursor polymers, liquid telechelic elastomers bearing the two types of antagonist functions on the same chain.

Preliminary results reveal that these crosslinked polymers may have interesting potential properties in the domain of adhesion (French Patent, 1982).

References

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