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SYNTHESIS OF STATISTICAL NETWORKS FROM LIQUID POLYBUTADIENE—IV

INFLUENCE OF CROSSLINKING AGENT

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Abstract—The synthesis of statistical macromolecular networks is achieved from liquid polybutadiene as precursor polymer with difunctional crosslinking agents bearing two hydrogenosilane groups. The properties of the network (extractable polymer, equilibrium swelling degree, uniaxial compression modulus) are strongly influenced by the structure of the crosslinks. Aromatic type structures are best suited to obtain high modulus networks which can be used for applications in the field of composite materials.

INTRODUCTION

The synthesis of statistical macromolecular networks is achieved from polybutadiene as precursor polymer (PB) with a difunctional crosslinking agent bearing two hydrogenosilane groups. These groups react with the pendant double bonds of the precursor polymer [1–3]. The precursor homopolymer is in liquid form (molecular weight, 2000–8000 g/mol) with mainly 1,2 structure (over 50%). The physical properties of a network depend on the crosslink functionality and on the molecular weight of the elastic chains: in this paper, these two parameters are directly dependent on the ratio R (no. of pendant double bonds/no. of Si–H). If the reaction is achieved in a stoichiometric condition (R = 1), every terminal carbon atom of every pendant double bond gives rise to a crosslink. The classical meaning of elastic chain is no longer significant because every chain is replaced by a short segment of about ten atoms according to the initial structure of the PB. The precursor polymer can be considered as a macromolecular plurifunctional crosslink with functionality $\bar{f}$ defined by the relationship:

$$\bar{f} = f_S . \overline{DP}_n$$

f_S, with value between 0.5 and 0.75, is characteristic of the precursor polymer microstructure. The properties of the network and the mesh size will be dependent on the physicochemical structure of the linking agent. The results described here agree with this hypothesis, as shown by measuring the uniaxial compression modulus E_G and the volume swelling degree G. The present paper has been focused on the influence of the following crosslinking agents: M'_2 type disiloxane such as dihydrogeno-1,3-tetramethyl-1,1,3,3-disiloxane; $M'D_4M'$ or dihydrogeno-1,11-dodecamethyl-1,1,3,3,5,5,7,7,9,9,11,11-hexasiloxane; an α,ω-hydrogenosilane alkane $R(SiH)_2$: 1,6-*bis*(dimethylsilyl)hexane; an aromatic adduct $Ar(SiH)_2$: 1,4-*bis*(dimethylsilyl) benzene, and a telechelic hydrogenosilane polymer: $PB(SiH)_2$. The latter could be used as precursor polymer and as a difunctional crosslinker simultaneously [2]. The crosslinking occurs by reaction between the pendant double bonds statistically distributed along the polymer backbone, and the Si–H groups. Three types of networks have been obtained. A type: Reaction between a crosslinking agent of the above series and a non-telechelic PB. Pendant chains may be present to some extent. B type: Network obtained by autocrosslinking of a liquid telechelic $PB(SiH)_2$. The ends of the chains give rise to crosslinks. Pendant chains are not present. C type: Crosslinking of a telechelic PB with a linking agent of the above series. The ends of the precursor polymer chain and the terminal carbon atom of the pendant double bonds give rise to crosslinks.

EXPERIMENTAL

The synthesis of the prepolymers and of the networks, and the determination of the equilibrium swelling degree have been described already [3].

Uniaxial compression modulus

E_G has been measured by means of apparatus described by Van De Kraats [4] and Donkersloot [5]. In this paper, E_G is characteristic of the non-swollen network.

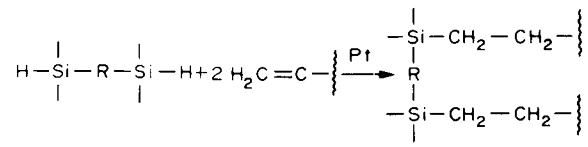
Synthesis of $R(SiH)_2$ (**I**) *and* $Ar(SiH)_2$ (**II**)

Dibromohexane (0.5 mol) or 1,4-dibromobenzene are dissolved in 400 ml THF. Mg (1 mol) is added and the mixture is heated, with magnetic stirring, for 24 hr at 67°. After cooling to 20°, 1 mol of dimethylchlorosilane is added dropwise. After heating to 40° for 4 hr, the solution is filtered off. The precipitate is washed twice with THF. The soluble fractions are collected and THF is distilled. The residue is dissolved in ether. This solution is treated three times with distilled water and dried over calcium sulphate. Ether is then distilled. The silyl derivatives (**I**) and (**II**) are separated by fractional distillation under reduced pressure. (**I**) T_E (2 mm) = 57°; yield = 65%. (**II**) T_E (1 mm) = 70°; yield = 54%.

The products are characterized by the usual methods. ^{1}H-NMR (sol. CCL_4; ref. TMS) 0.2 ppm: $Si(CH_3)_2$; 0.6 ppm: $Si\text{-}CH_2$; 1.2 ppm: $(CH_2)_4$; 4.1 ppm: Si–H; 7.0 ppm: aromatic ring. I.R.: 2100 cm^{-1}: Si–H. Elemental analysis (**I**): C% 61.56, H% 9.25, calc. 61.78, calc. 9.33. (**II**): C% 59.28, H% 12.67, calc. 59.32; calc. 12.94.

RESULTS AND DISCUSSION

The crosslinking reaction is based on the classical addition of a hydrosilane (hydrosilylation) onto a vinyl pendant double bond [1] of the polymer precursor according to Scheme 1:



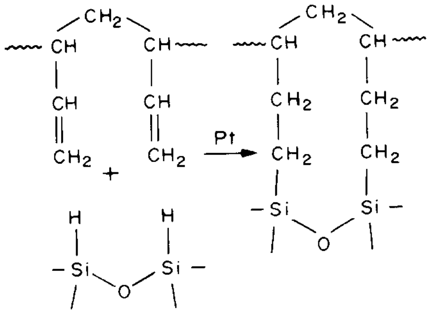
Scheme 1

The three types of networks A, B and C are shown on Fig. 1.

As shown by Fig. 1, the crosslinking reaction is either an "end-linking" type mechanism if the polymer precursor is a telechelic material (B), or a usual addition mechanism on the double bonds along the polymer backbone (A) or both (C). The three types of networks are different from the point of view of the crosslink density and the presence of free end chains. The probability of side reactions may be of considerable importance: they depend on the structure of the coupling agents which can be classified as follows:

$$M'_2 > M'D_4M' \simeq R(SiH)_2 > Ar(SiH)_2$$

^{1}H-NMR of the soluble fraction extracted from the network obtained with M'_2 sample shows the presence of -$Si(CH_3)_2$-O-$Si(CH_3)_2$ type units. The initial CH_3 doublet at 0.2 ppm, due to its coupling with the α-proton on the silicon atom disappears and turns into a singlet located also at 0.2 ppm. The multiplet at 4.7–5.0 ppm which corresponds to the 1,2 structure of PB disappears also. Taking into account the bond angles and the interatomic distances, this result confirms the hypothesis of a possible M'_2 addition on two successive double bonds of the same PB chain. As observed on molecular models, as soon as a Si–H group is added to a double bond, the second Si–H unit is in a favourable position and close enough to the neighbouring double bond to give rise to a cyclic structure according to Scheme 2.



Scheme 2

Table 2. E_G values as a function of coupling agent

	E_G (N/cm^2)			
$\bar{M}_n$	M'_2	$M'D_4M'$	$R(SiH)_2$	$Ar(SiH)_2$
2000	167	323	340	880
3000	227	336	325	900
4000	162	214	—	910
5000	172	330	—	960
8000	293	271	—	950

This configuration does not exist as soon as the length of the bridge ($M'D_4M'$, $R(SiH)_2$, $PB(SiH)_2$) increases or as soon as the molecule exhibits either some important steric hindrance or a rigid backbone as in $Ar(SiH)_2$. This result is confirmed by measuring the fraction of soluble polymer (P_E) (Table 1).

The P_E values are systematically higher when the networks have been obtained with M'_2 as compared to those obtained with $M'D_4M'$ and even more so with $Ar(SiH)_2$. In this latter case, the fraction of soluble polymer extracted is close to zero. We can nevertheless observe that, for precursor polymers with $\bar{M}_n > 3000$, P_E decreases. This result can be explained by the simultaneous presence of chemical linkages and physical linkages due to entanglement of PB precursor chains [6]. The equilibrium swelling degree G is little influenced by this phenomenon.

Values of the uniaxial compression modulus E_G as measured on the network are shown in Table 2. Here again one can observe an important increase of the modulus in relation to the structure of the linking agent. For identical experimental conditions (same $\bar{M}_n$, R) the networks obtained with M'_2 exhibit lower modulus than those found with other linking agents. This result can be explained by the influence of side reactions similar to that shown above (Scheme 2) with the possibility of cycle and pendant chain formations, which do not take part in the network formation. For $Ar(SiH)_2$ loops can also be formed but because of the linking agent structure, four butadiene units are necessary. Scheme 3 represents such a loop in orthogonal projection on the plane of the polybutadiene backbone. This representation is obtained from molecular models of the "Courtauld atomic models" type. The aromatic protons as well as those of the two methyl groups of each silicon atom are not represented on the Scheme for clarity.

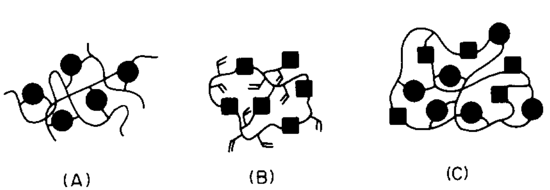
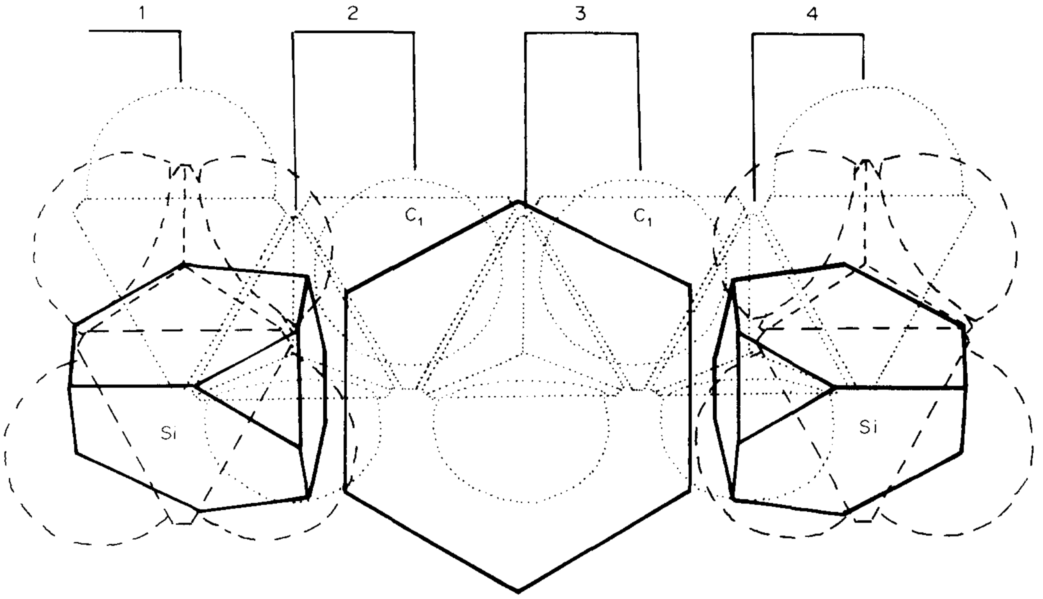


Fig. 1. Different network types: (■) crosslink by "end-linking" reaction; (●) crosslink along the chain.

Table 1. Measure of the fraction of extractable polymer P_E and of the equilibrium swelling degree G as a function of linking agent (R = 1)

$\bar{M}$ of polymer precursor	P_E (%)				G			
	M'_2	$M'D_4M'$	$R(SiH)_2$	$Ar(SiH)_2$	M'_2	$M'D_4M'$	$R(SiH)_2$	$Ar(SiH)_2$
2000	3.16	1.84	1.75	~0	1.51	1.51	1.40	1.15
3000	3.50	1.80	1.60	0	1.41	1.41	1.52	1.20
4000	2.73	1.05	—	0	1.67	1.57	—	1.10
5000	2.06	1.29	—	0	1.47	1.42	—	1.18
8000	2.01	1.43	—	0	1.53	1.48	—	1.07



Scheme 3. Loop structural unit during crosslinking.

The double bonds carried by these loops situated on the C_1 carbon are used subsequently to create crosslinking centres so that these loops can be considered as a network mesh and not as a defect which could affect mechanical properties. This view is confirmed by the high values of the E_G modulus which have values above 900 N/cm^2 and by the fraction of extractable polymer being close to zero.

CONCLUSION

Properties (extractable fraction, equilibrium swelling degree, uniaxial compression modulus) of statistical networks obtained through hydrosilylation of the pendant double bonds of a 1,2-polybutadiene sample using a linking agent of the hydrogenosilane type, are strongly influenced by the structure of the latter. Depending on its molecular weight, the rigidity of the molecule and the steric hindrance around the silicon atom, side reactions giving rise to cyclic products and to polymer with large extractable fraction are more or less important. Thus it is found that aromatic type structures are best suited to obtain high modulus networks with equilibrium swelling degrees close to 1 and no extractable polymer. Networks thus obtained can be used for applications in the field of composite materials.

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Résumé—La synthèse de réseaux statistiques est réalisée à partir de polybutadiène précurseur liquide, par hydrosilylation des doubles liaisons pendantes avec des molécules difonctionnelles porteuses de deux fonctions hydrogénosilane. Les propriétés des réseaux (taux de gonflement, module d'élasticité en compression uniaxiale) sont fonction de la structure de l'agent de pontage. Des structures de type aromatique s'avèrent les plus adaptées pour l'obtention de réseaux à module élevé, susceptibles d'applications dans le domaine des matériaux composites.