

Synthesis of Statistical Networks from Liquid Polybutadiene.

V. Synthesis and Adhesive Properties of 1,2-Polybutadiene Networks

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Synopsis

A series of 1,2-polybutadiene networks was prepared either by endlinking reaction of telechelic liquid precursors or/and by crosslinking with disilyl compounds. Transparent materials were obtained and used as adhesives in glass assembly mainly. The shear resistance at break was found to be higher compared to conventional vulcanized elastomers.

INTRODUCTION

The performance of an adhesive is a function of the chemical structure and the physical properties of the polymeric base from which it is made.

Rubber adhesives and related elastomeric polymers are used quite widely. To ensure technological applications, polydienes have to be vulcanized, i.e., crosslinked. To improve their adhesive properties, polar groups can be added to the polymer chain. For adhesion to a glass substrate, the common bonding technique consists in a previous surface treatment with coupling agents capable of forming chemical bonds. Silane reagents are widely employed. Another way of adhesion promotion may be chemical modification of the polymer.

In this article we report the synthesis and adhesive properties of polybutadiene crosslinked *in situ* with dihydrogenosilane compounds.¹ The polybutadiene homopolymer precursor, prepared by living anionic process, was in a liquid form (molecular weight of 1500–8000 g/mol) with mainly 1,2 structure (over 75%).

The networks were obtained either by thermal crosslinking of telechelic polybutadienes or by reaction of polybutadiene with a disilyl compound^{2,3} in the presence of a platinum catalyst. The combination of these two syntheses, i.e., crosslinking of α,ω -functionalized polybutadienes with difunctional hydrogenosilanes was also examined.

Several crosslinkers with hydrogenosilane functions were used: 1,3-dihydrogeno-1,1,3,3-tetramethyldisiloxane (M_2), 1,4-bis(dimethylsilyl)benzene (DMSB) or 1,6-bis(dimethylsilyl)hexane (DMSH).

The adhesive properties of these networks have been tested in simple overlap joints. Glass was mainly used as the substrate. Crosslinking reaction

and adhesion took place simultaneously by the effect of temperature and platinum catalyst.

EXPERIMENTAL

Synthesis of Liquid Homopolybutadiene²

Low molecular weight polybutadienes were prepared at -50°C by a now classical anionic polymerization procedure. The solvent was THF, the initiator was lithium-naphthalene, and the polymerization was carried out in an argon atmosphere. The polymer was isolated by precipitating it with methanol from its solution and drying it at 40°C under vacuum to constant weight.

The molecular weight and the microstructure of the polybutadiene were determined by GPC and $^1\text{H-NMR}$, respectively. The liquid polymers thus prepared ranging in number average molecular weight from 1500 to 8000 g/mol with low polydispersity, contained at least 75% of 1,2 units.

Synthesis of Telechelic Prepolymers³ (DMSPB)

A solution of dimethylchlorosilane in THF was added dropwise under energetic stirring to the "living" polybutadienyldilithium adduct at -50°C . The slow addition was followed by 2 h additional stirring at -50°C . Afterward the solution was concentrated under vacuum. The difunctionalized polybutadiene was precipitated with methanol, redissolved in benzene, precipitated again, and dried under vacuum for several days.

Synthesis of Crosslinking Agents

1,3-Dihydrogeno-1,1,3,3-tetramethyldisiloxane (M_2) was a commercial product (Wacker silane) used as supplied. 1,4-bis(dimethylsilyl)benzene (DMSB) and 1,6-bis(dimethylsilyl)hexane (DMSH) were prepared in two steps from corresponding dibromo compounds and dimethylchlorosilane. A 1-L three-necked flask was equipped with an efficient reflux condenser to an argon source. It was fitted with a motor stirrer and a dropping funnel. The flask was blanketed with argon and then charged with 1.1 mol of magnesium chips and 250 mL of dry THF. As this suspension was rapidly stirred, a mixture of 0.5 mol of *p*-dibromobenzene or 1,6-dibromohexane dissolved in 400 mL of dry THF was added dropwise. Then the resultant mixture was treated under reflux for 20 h.

In the second step, the hydrosilylation reaction was achieved by adding 1.1 mol dimethylchlorosilane to the above solution and heating the resultant mixture under reflux for 6 h. The addition is usually made at room temperature but can be done at any temperature under 35°C .

After cooling and filtration, 250 mL of ether were added to the solution. The ether layer was separated, washed with water, and then dried with calcium chloride. The ether was removed by evaporation and the disilyl compound that remained was distilled under reduced pressure. The yield was 62%. The products were characterized by usual techniques such as IR and $^1\text{H-NMR}$ spectroscopy and elemental analysis.

Synthesis of Networks

The networks were prepared in bulk at 70–120°C by reaction of the polymer with the crosslinking agent in the presence of platinum catalyst.² The appropriate amount of crosslinker was taken so that the ratio R of pendent bonds to silane hydrogen groups was equal to 1.

Joint Formation

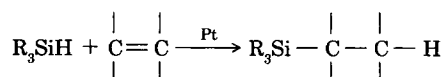
Glass plates (50 × 25 × 6 mm) used as substrate were degreased with ethanol just before use. A simple lap joint (overlap area = 6.25 cm²) was formed by depositing about 0.1 mL of the above mixture between two plates. A special device allowed exact positioning of the different parts of the joint. A spring set to 1 kg/cm² pressed on the center of the overlap area. The test samples were prepared by heating the whole assembly for 24 h at 70–120°C. Then the temperature was decreased slowly to room temperature.

Joint Breaking

The shear strength of all joints was measured on a Zwick testing machine, Model Z 13 with a crosshead separation speed of 2 mm/mn. At least 10 joints were tested for each network. \bar{F} and F_{\max} (Table III) are the average value and the maximum value respectively of the tensile shear strength at break in daN/cm².

RESULTS AND DISCUSSION

Crosslinking of polydienes by means of terminal dihydrogenosilane oligomers involves the well-known addition reaction⁴⁻⁶ of a hydrosilane function R_3SiH onto a double bond according to the following scheme:



Hence three types of networks, illustrated in Figure 1, were obtained,⁷ depending on the chemical functions provided by the precursor and crosslinker as well. They differ essentially by the number of free end chains, of pendent double bonds, and by the packing of the junction points.

The A-type network is obtained without addition of crosslinker by intermolecular crosslinking of telechelic polybutadienes. In that case, the junc-

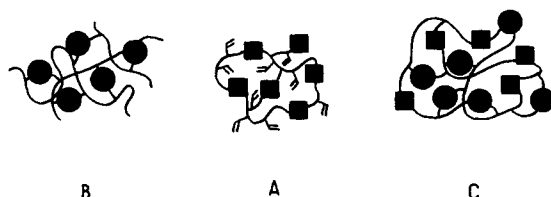


Fig. 1. Different network types: (■) crosslink by "end-linking" reaction; (●) crosslink along the chain.

TABLE I
Glass Transition Temperature of Linear and Crosslinked Polybutadienes

Polybutadiene sample	Linear		Crosslinked		
	Homopolymer	Telechelic	A-type	C-type ^b	C-type ^c
T_g (°C) ^a	-47	-30	-5	+23	+66

^a DSC 16°/mn.

^b Crosslinking agent M_2 .

^c Crosslinking agent DMSB.

tion points are mainly located at the chain ends; however, loops may be formed by intramolecular combination.

By reaction of bis(hydrogenosilyl) compounds with polybutadiene homopolymer a B-type network is formed, where the end chains remained free, i.e., pendent.

Finally, in the C-type network combining the two previous reactions, the junction points are formed both by the chain ends and terminal carbon atoms of the pendent double bonds of elementary backbone.

The physical properties and consequently the adhesive properties of the different types of networks are greatly influenced by the number of crosslink sites. This is typically shown in Table I by the change in the glass transition temperature T_g . More physical data are given for C-type networks only (Table II) which exhibit interesting performances from an adhesive point of view, as shown later in the text. These networks present a good thermal stability as shown by the thermogravimetric diagram (Fig. 2).

Total decomposition occurs around 500°C. The adhesive properties of polybutadiene networks are reported in Table III. Glass to glass assemblies were optically transparent and colorless. Some preliminary works have shown that the molecular weight \bar{M}_n of B- and C-type networks precursors has no influence on the shear resistance at break in the range under investigation. For A-type networks (no crosslinker used), however, when \bar{M}_n increases the adhesive properties decrease.

The parameters here under consideration are the chemical nature of the crosslinking agent and the ratio R of the *pendent* double bonds over Si—H groups. (1.2 structure of the polymer only is suitable for crosslinking, i.e., pendent double bonds.^{2,3}) In the present work, $R = 1$, as mentioned in Experimental except for A-type networks where R is directly correlated with the molecular weight of the prepolymer. Hence for $\bar{M}_n = 2500$ (Table III), $\bar{R} = 18$.

TABLE II
Physical Properties of C-type Networks

Hardness: Shore D	75
Thermal stability	300°C
Compression modulus	100 daN/cm ²
Aspect	transparent, colorless
Density	0.96
Swelling degree	1.07-1.15
Extractable	0
Young modulus	8000 daN/cm ²

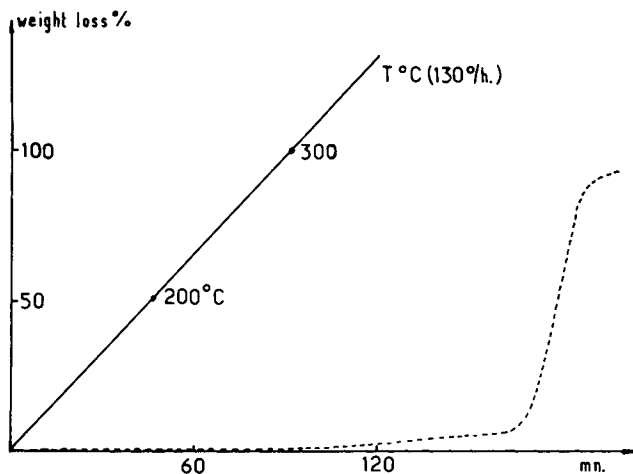


Fig. 2. Thermogravimetric diagram of C-type network.

It can be seen from Table III that B- and C-type networks have higher shear resistance at break than other elastomeric based adhesives according to literature data.⁸ This was found for various joints involving high energy surfaces like glass and aluminum. The break resistance F is strongly influenced by the crosslink density and the nature of the 3-dimensional junction points. A change in the molecular weight of the crosslinking agent, in the rigidity of the molecule, and in the steric hindrance around the Si atoms gives rise to cyclic structures,⁷ which modify the adhesive properties. The best values were obtained with aromatic crosslinkers. In all cases the rupture of the joint was of cohesive nature (failure within the adhesive).

CONCLUSION

Due to their good adhesive properties¹ toward various adherents, networks obtained this way can be used as matrix in the preparation of reinforced materials. Composite containing up to 90% of fillerlike glass fibers, carbon fibers, powdered metals, and glass beads (syntactic foam) have already been proposed, and their physical properties will be presented in a forthcoming paper.

TABLE III
Shear-Resistance at Break of Various Joints Bonded with Polybutadiene Networks^a

Network type	Crosslinking agent	\bar{F} (daN/cm ²)	F_{max}	Substrate
A	DMSPB	15	22	Glass/glass
B, C	DMSH	60	80	Glass/glass
B, C	M ₂	70	82	Glass/glass
B, C	DMSB	100	145	Glass/glass
C	DMSB	62	65	Glass/Al
C	DMSB	75	80	Al/Al

^a Molecular weight of prepolymer, $\bar{M}_n = 2500$.

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