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Polybutadiene Modification: Reactions of Halogen-Containing Polybutadienes with Organolithium Compounds

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ABSTRACT

Polybutadiene (PB) can be easily halogenated by reaction with iodine chloride or bromine in tetrahydrofuran. The resulting glassy polymers were reacted with *n*-butyllithium, *sec*-butyllithium, and polystyryllithium in THF. Iodochlorinated PB gave a polybutadiene with a different *cis/trans* ratio with *n*-BuLi. The reformation of PB was accompanied by partial crosslinking. The reaction probably involved a halogen-metal exchange followed by intra- and intermolecular elimination of Li halide. With brominated PB, both coupling and elimination took place. With *sec*-BuLi, an allylic iodine derivative was obtained from iodochlorinated PB, probably by dehydrochlorination. The iodinated intermediate can easily undergo a coupling reaction with further *sec*-BuLi. Both iodochlorinated and brominated polybutadienes gave graft copolymers by reaction with polystyryllithium in THF. Grafting was always accompanied by gel formation.

Halogenated polybutadienes constitute potentially useful intermediates for obtaining polybutadienes containing other functional groups along the backbone [1] or various graft copolymers. Depending on the degree of chemical modification and the nature of functional groups or grafts, a range of new polymers with interesting properties can be synthesized.

In the first stage of a research program on polybutadiene modification, reactions of iodochlorinated and brominated polybutadienes with organolithium compounds were investigated. Two polybutadienes were used as starting materials: a predominantly *cis*-1,4-polymer synthesized with a Ziegler-Natta (Al/Ti) catalytic system, and a predominantly 1,2-polymer synthesized with a diglyme-modified organolithium catalyst. The main properties of the two polybutadienes are given in Table 1.

TABLE 1. Properties of Polybutadienes

	<i>cis</i> -1,4-PB	1,2-PB
Microstructure:		
<i>cis</i> -1,4, %	92	26
<i>trans</i> -1,4, %	3	14
1,2, %	5	60
\bar{M}_n , g/mol	150,000	7,500
\bar{M}_w/\bar{M}_n	2.2	1.1

HALOGENATED POLYBUTADIENES

Halogenation reactions were carried out in tetrahydrofuran (THF) at 0°C by adding dropwise stoichiometric amounts of iodine monochloride or bromine as solutions in THF to a stirred solution of polymer. As is known [2], elemental bromine reacts with THF but at a much slower rate than with polybutadiene. This is clearly illustrated by the change in optical density of bromine solutions in THF in the presence and in the absence of polybutadiene (Fig. 1). Also, halogenation yields (with both ICl and bromine) were always close to theoretical.

Halogenated polymers were separated from solution by precipitation with dry isopropanol and then dried in vacuum at 40°C. The reaction products were characterized by elemental analysis and infrared spectroscopy. Glass transition temperatures were determined by differential scanning calorimetry and wide band NMR. Thermal stability was determined by thermogravimetry. It can be seen from the data given in Table 2 that halogenated polybutadienes are thermoplastic materials

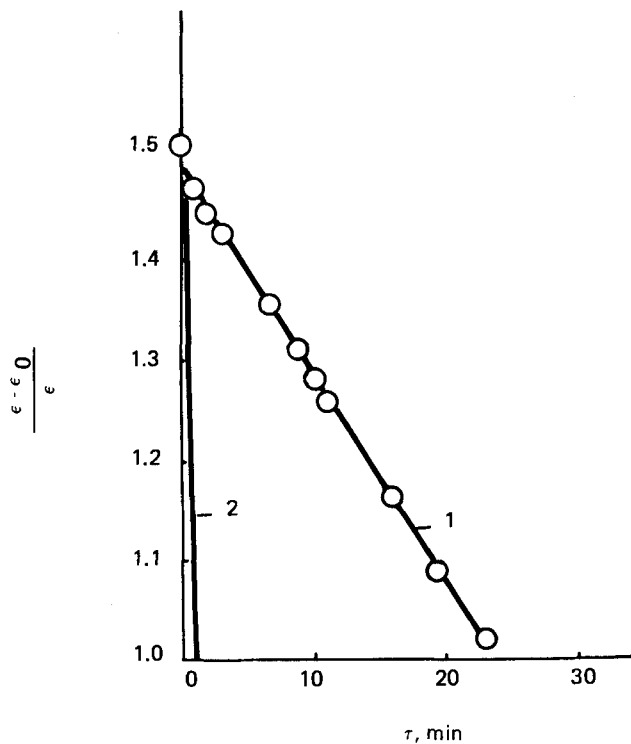


FIG. 1. Rate of bromine consumption in tetrahydrofuran in the absence (1) and in the presence (2) of polybutadiene.

TABLE 2. Properties of Halogen-Containing Polybutadienes

	Iodochlorinated		Brominated 1,2-PB
	cis-1,4-PB	1,2-PB	
Elemental analysis:			
Iodine, %	50.8	51.1	-
Chlorine, %	14.6	14.8	-
Bromine, %	-	-	72.3
T_g by DSC, °C	32	48	38
T_g by NMR, °C	33	47	39

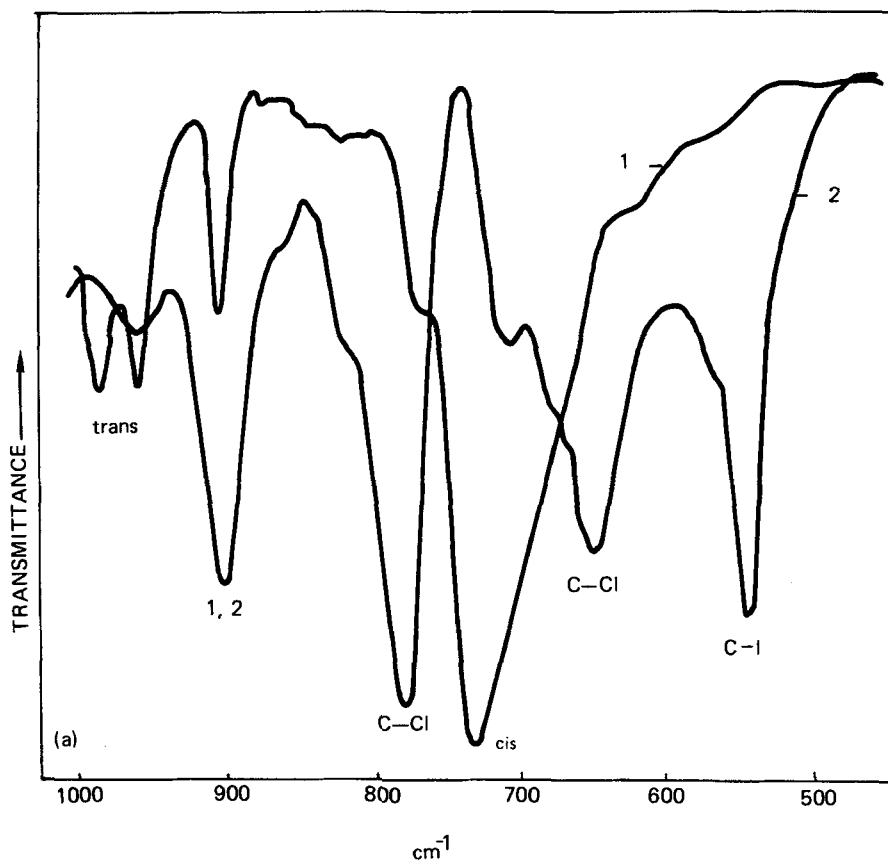


FIG. 2. IR spectra of initial (1) and iodochlorinated (2) polybutadienes. (a) cis-1,4-Polybutadiene. (b) 1,2-Polybutadiene.

with T_g 's above room temperature. The degree of halogenation of the reaction products was practically total, as seen from the IR spectra of halogenated polybutadienes given in Figs. 2 and 3.

Bromination and iodochlorination reactions thus proceed through halogen addition to the main chain or side chain double bonds in the usual manner.

Halogenated polybutadienes, regardless of the microstructure of the initial polymer, were insoluble in a wide range of usual solvents (benzene, toluene, butyl acetate, methyl ethyl ketone, dioxane) including a series of halogenated solvents such as carbon tetrachloride, chloroform, dichloroethane, trichloroethylene, tetrachloroethylene, and bromoform. In dimethylformamide the polymers dissolved with decomposition, but were totally soluble in THF.

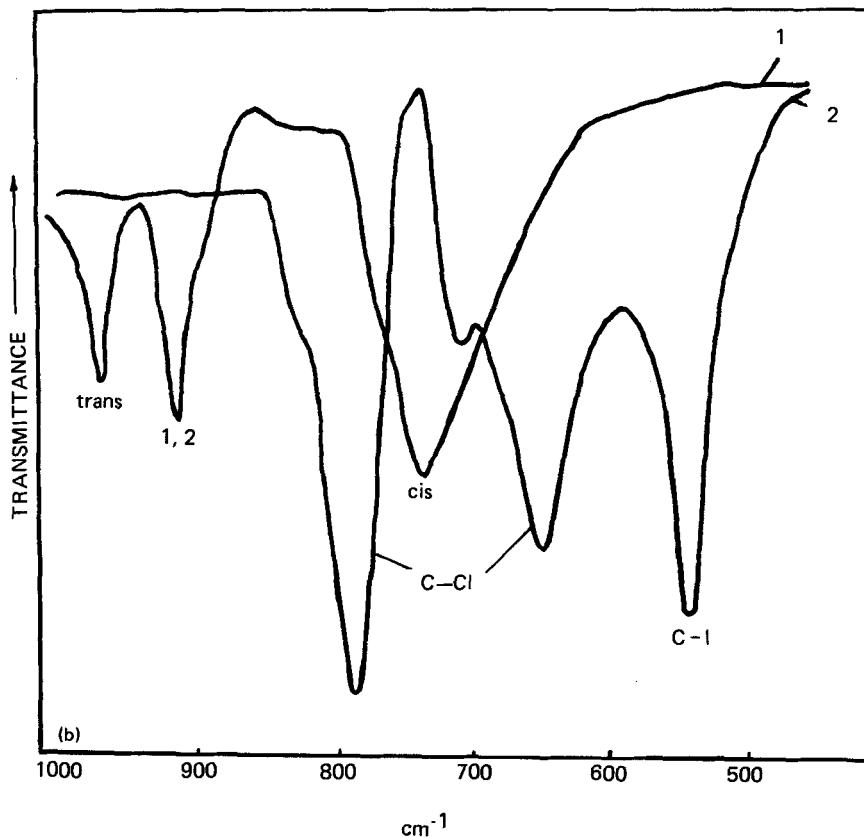


FIG. 2 (continued)

The thermogravimetric scan of iodochlorinated *cis*-1,4-polybutadiene is given in Fig. 4. It is seen that thermal decomposition begins below 100°C and then accelerates strongly. The first halogen to leave the molecule is iodine, and only after its virtually total elimination is chlorine lost, as evidenced by the distinct step in the TG trace.

Halogenated polybutadienes slowly eliminate halogen, even at room temperature. This is accompanied by a change of color from colorless or pale yellow to pink or brown. Partial crosslinking also occurs, with a corresponding loss of solubility. In all cases iodochlorinated polybutadienes were, somewhat surprisingly, more stable than the brominated ones.

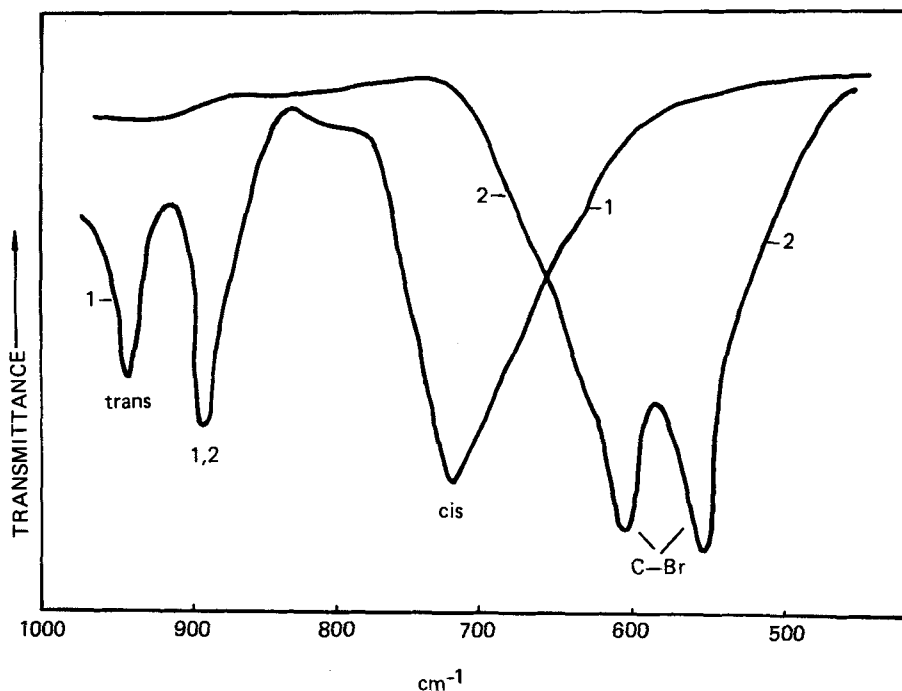


FIG. 3. IR spectra of initial (1) and brominated (2) 1,2-polybutadiene.

REACTIONS WITH *n*-BUTYLLITHIUM

Halogenated polybutadienes were dissolved in freshly distilled and dried THF under a blanket of purified argon. A solution of *n*-butyllithium, after cooling to 0°C, was added dropwise under stirring until the stoichiometric amount of organolithium compound was reached. The polymeric reaction products were recovered from solution by precipitation with isopropanol, dried in vacuum, and characterized by elemental analysis, IR, and ¹H-NMR spectroscopy (60 MHz).

For both iodochlorinated and brominated polybutadienes, elemental analyses showed the total absence of halogens after reaction with a stoichiometric amount of *n*-BuLi with respect to total halogen.

The reaction product between iodochlorinated *cis*-1,4-polybutadiene (I) and *n*-BuLi consists of 80% soluble polymer and 20% gel. Infrared (Fig. 5a) and NMR (Fig. 5b) spectra of the soluble fraction gave no evidence of any coupling reaction of the organolithium com-

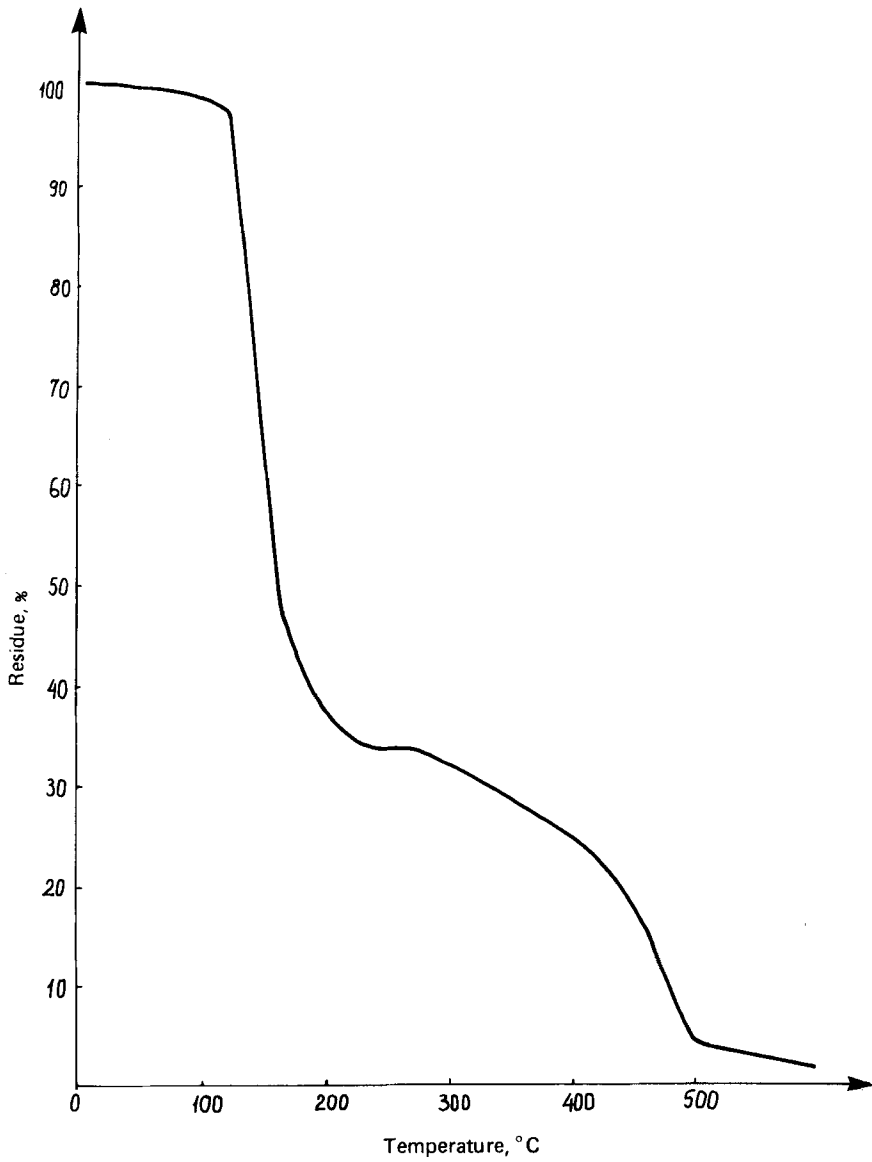


FIG. 4. TGA trace of iodochlorinated cis-1,4-polybutadiene.

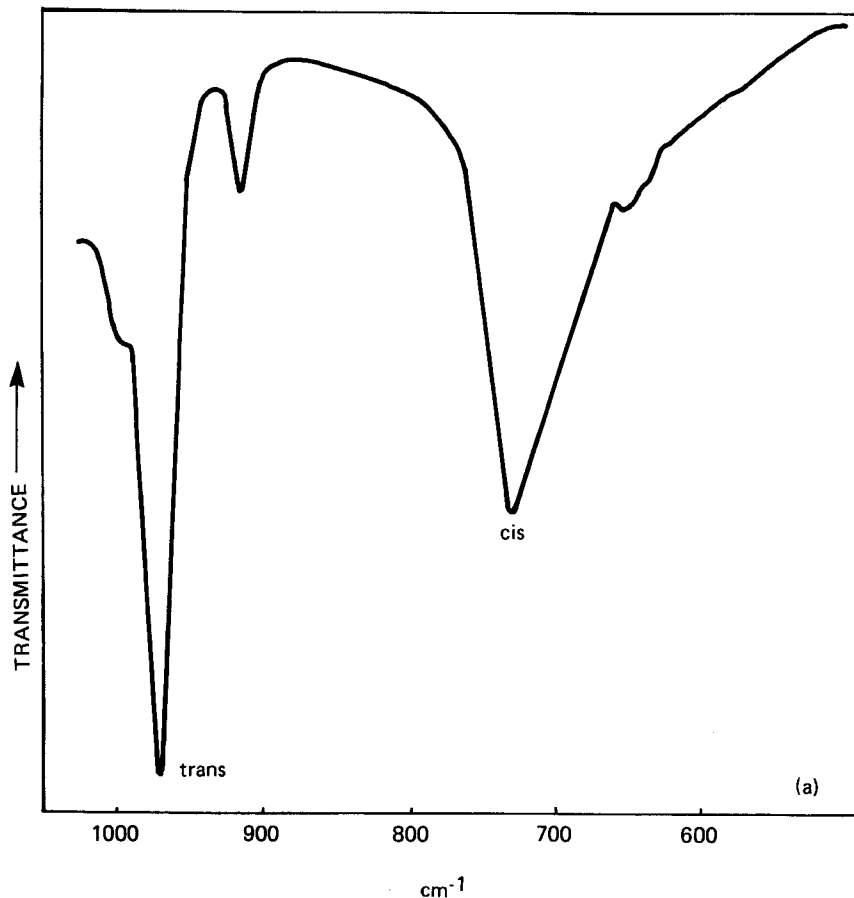


FIG. 5. IR (a) and NMR (b) spectra of the soluble product of the reaction between iodochlorinated cis-1,4-polybutadiene and n-butyl-lithium.

pound with the halogenated polymer. The main reaction seems to be an elimination conducive to a reformation of polybutadiene with a different microstructure (48% cis-1,4, 47% trans-1,4, and 5% 1,2 units). A side reaction leads to the formation of crosslinks. The probable reaction mechanism involves a halogen-metal exchange [3], followed by elimination of lithium halide. If the elimination is intramolecular, a polybutadiene with a cis/trans ratio of ~ 1 results (III), whereas if the reaction takes an intermolecular course, crosslinked polymer (IV) is obtained. The proposed sequence of reactions is

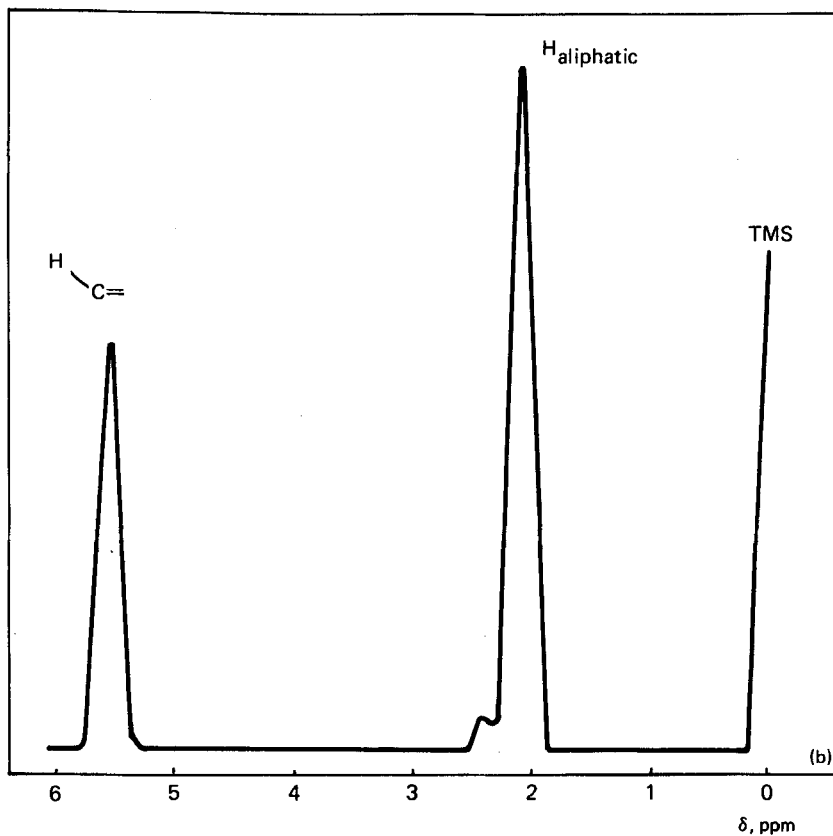
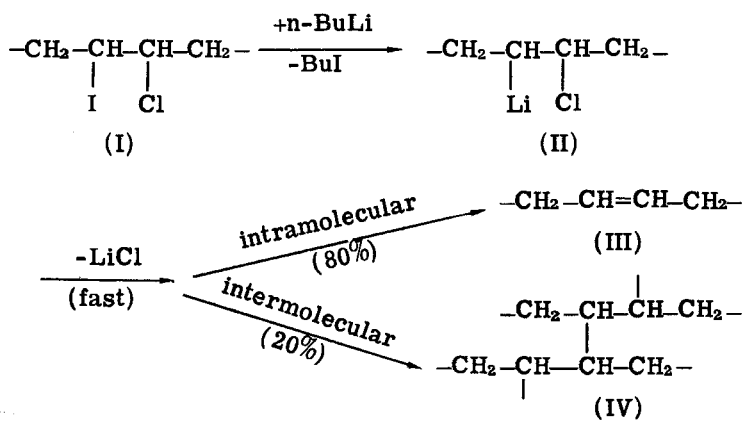


FIG. 5. (continued)



The lithiated intermediate (II) is probably very short-lived. Attempts to couple the intermediate with benzophenone or benzyl chloride have failed even when carried out at -78°C , as demonstrated by the lack of phenyl ring absorption in the UV spectra of the purified polymeric reaction product. Similarly, NMR spectra did not show the presence of, otherwise very easily identifiable, $-\text{Si}(\text{CH}_3)_3$ groups after treating the product of the reaction between (I) and $n\text{-BuLi}$ with

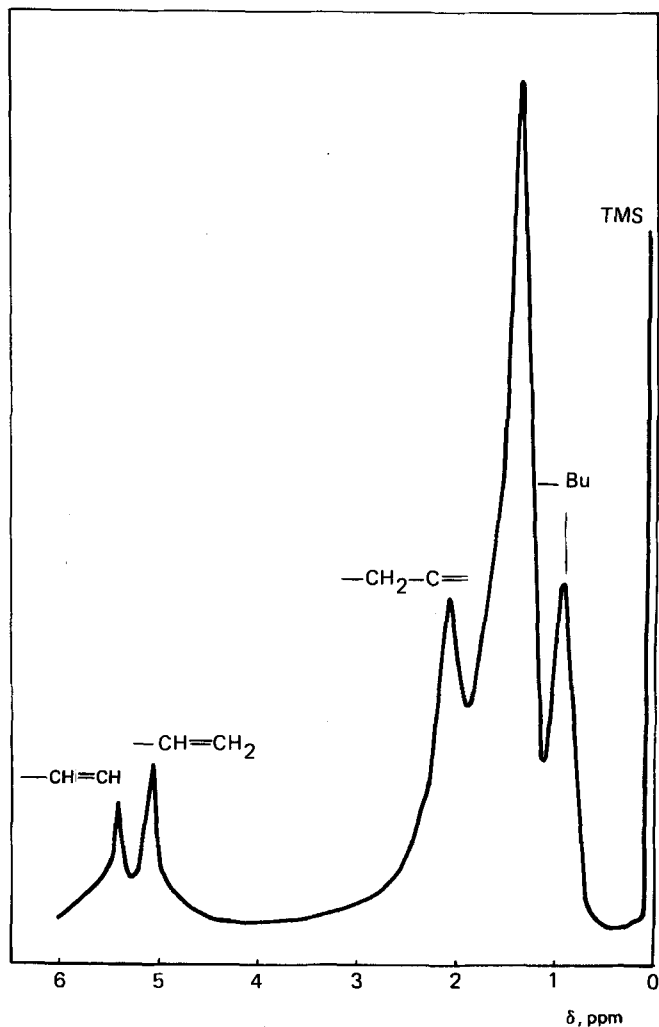
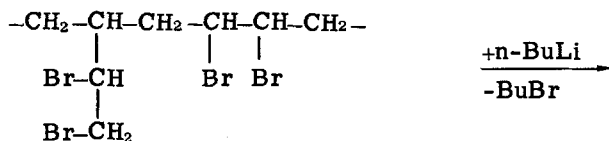


FIG. 6. NMR spectrum of the soluble product of the reaction between brominated 1,2-polybutadiene and n -butyllithium.

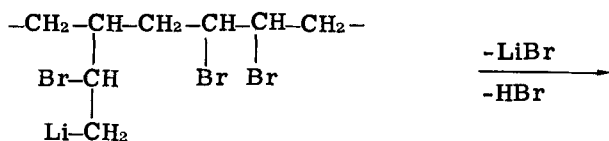
trimethylchlorosilane, again at Dry-Ice temperature. A very fast elimination of lithium chloride is normal, considering the neighboring presence of Li and Cl atoms in the molecule of the intermediate.

Iodochlorinated 1,2-polybutadiene showed a similar behavior in the reaction with *n*-BuLi. However, due to the relatively low content of 1,4 units and the lower *cis/trans* ratio in the initial polymer, no significant changes in the microstructure of reformed polybutadiene could be identified.

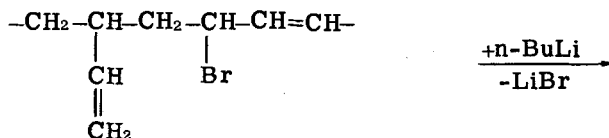
Brominated 1,2-polybutadiene (V) reacted in a slightly different manner with *n*-BuLi, yielding an unsaturated and partially alkylated polymer (VIII). The NMR spectrum of the reaction product (Fig. 6) tends to support the following reaction sequence:



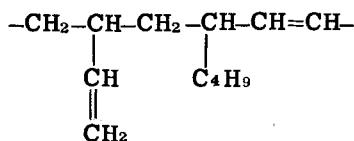
(V)



(VI)



(VII)



(VIII)

Hence, both elimination and coupling reactions seem to take place in this case.

REACTIONS WITH *sec*-BUTYLLITHIUM

The behavior of halogenated polybutadienes in reactions with *sec*-butyllithium is, under otherwise identical conditions, strikingly different from that shown in reactions with *n*-butyllithium. Thus, with half the stoichiometric amount of organolithium, iodochlorinated *cis*-polybutadiene yields an allylic iodine derivative (IX) as indicated by elemental analysis and the IR spectrum (see Fig. 7). This reaction product probably results by dehydrochlorination, a plausible reaction course since *sec*-BuLi is a stronger base than *n*-BuLi. The presence of the characteristic -OH bands in the IR spectrum given in Fig. 7 is a consequence of the hydrolysis undergone by the derivative (IX) in the presence of water purposely added to the isopropanol used for polymer precipitation. The reaction sequence is

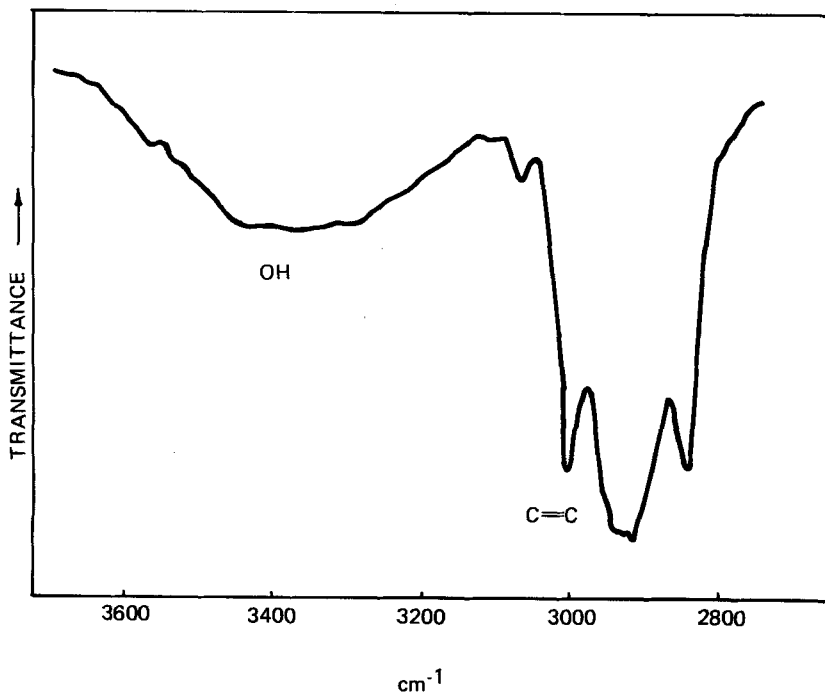
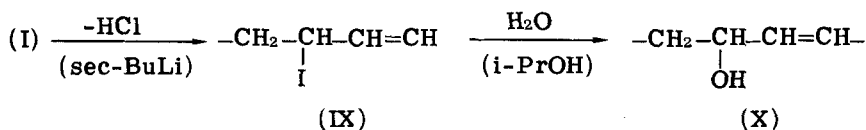


FIG. 7. IR spectrum of iodochlorinated *cis*-1,4-polybutadiene treated with half the stoichiometric amount of *sec*-butyllithium.

The NMR spectrum of polymer (XI) (Fig. 8) shows a virtually total substitution of iodine atoms by isobutyl groups.

REACTIONS WITH POLYSTYRYLLITHIUM

Polystyryllithium was synthesized by anionic polymerization of styrene with *n*-butyllithium in THF. The reactions of halogen-containing polybutadienes with polystyryllithium were carried out in a

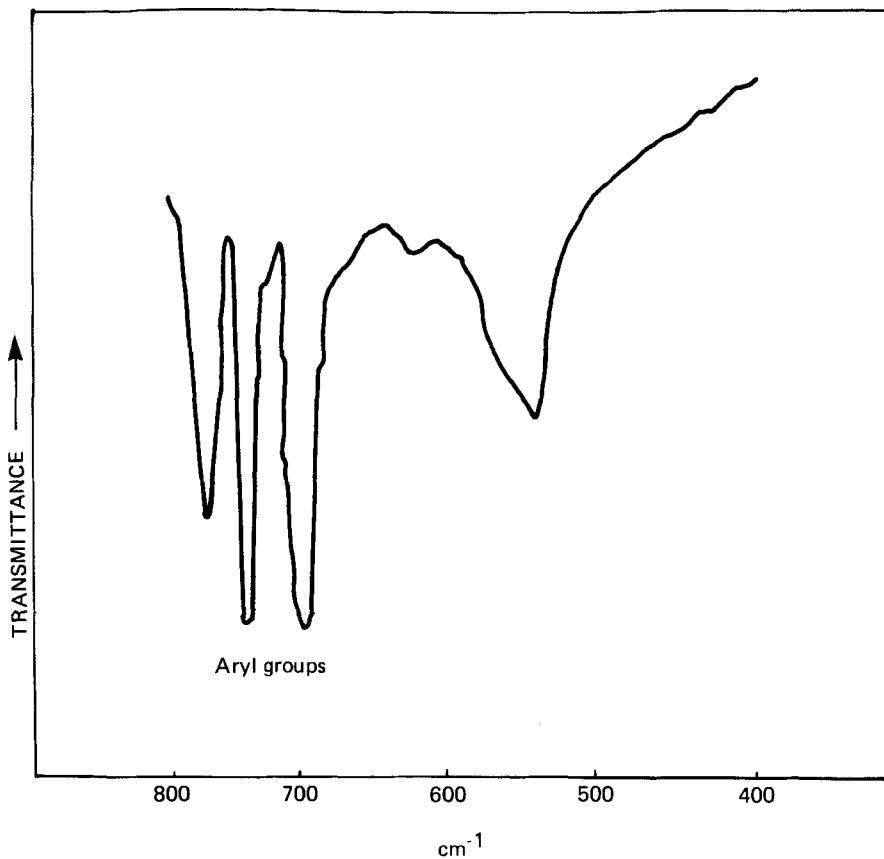


FIG. 9. IR (a) and NMR (b) spectra of the graft copolymer obtained by reacting iodochlorinated *cis*-1,4-polybutadiene with polystyryllithium.

manner similar to that described for reactions with alkyllithiums, with the difference that the reaction products were precipitated with a 1:1 mixture of isopropanol and acetone and then repeatedly extracted with pure acetone in order to remove unreacted polystyrene homopolymer. Polystyryllithium had a molecular weight of 5000 and a narrow molecular weight distribution.

Both iodochlorinated *cis*-1,4-polybutadiene and brominated 1,2-polybutadiene yielded graft copolymers whose IR and NMR spectra were practically identical due to the strong contribution of the phenyl rings contained in the side chains (Fig. 9). Grafting yield on (I) (determined gravimetrically) was 25%. The graft copolymer contained 5% gel. The copolymer based on (I) had two glass transition temperatures (determined by NMR): 38 and 92°C. Grafting was accompanied by a widening of the molecular weight distribution (see Fig. 10).

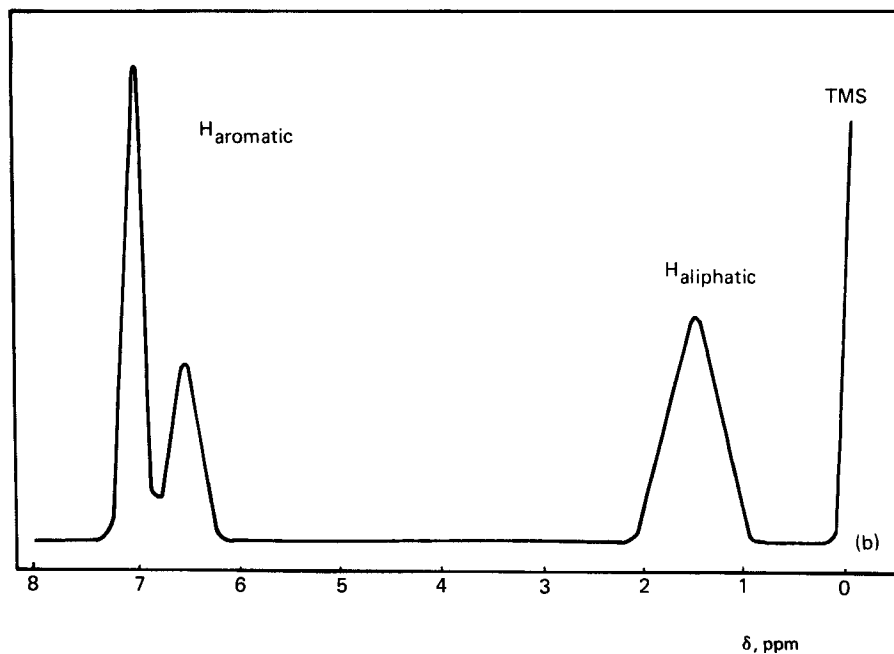


FIG. 9 (continued)

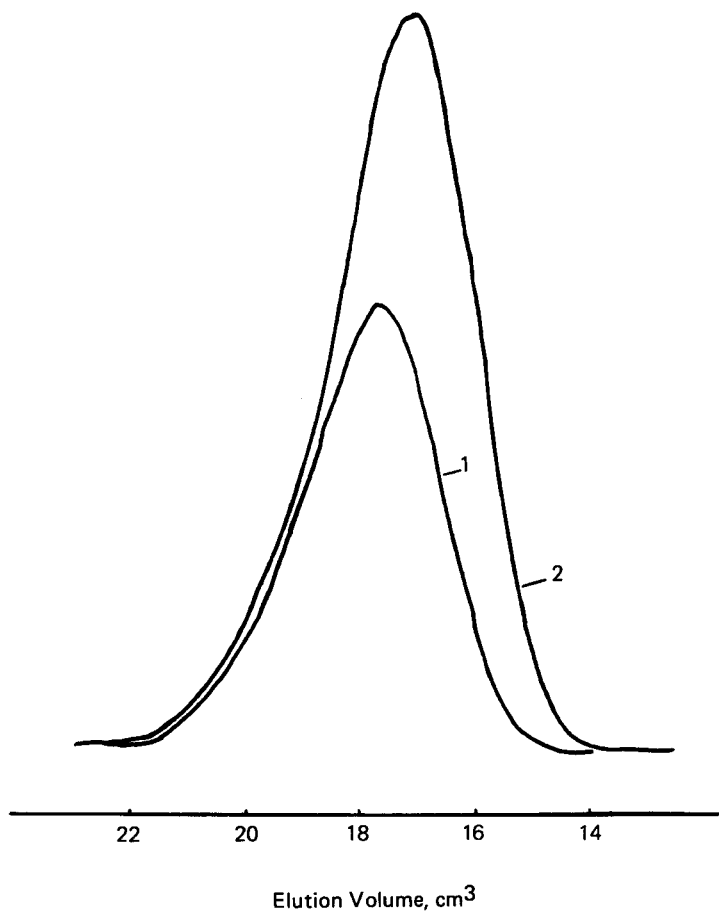


FIG. 10. Gel permeation chromatograms of cis-1,4-polybutadiene (1) and poly(butadiene-g-styrene) (2).

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