electron transfer with amine (AH), and monomer quenching (M). According to the very low values calculated for the different processes, sulfonyloxy ketones are rather poor radical photoinitiators in the absence of amine (comparative data for (2,2-dimethoxyphenyl)acetophenone (DMPA) and benzophenone (BP) are listed in Table II). On the other hand, these ketones are efficient sources of latent sulfonic acids,[8] because of the high reactivity of their triplet states ($k_\beta$, $k_e$, $k_d$) in the absence of acrylic monomers.

**Acknowledgment.** We are grateful to Dr. Rutsch (Ciba Geigy, Basel) for kindly donating authentic samples.

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# Polymerization of Monomers Containing Functional Silyl Groups. 8. Catalytic Hydrogenation of Poly(2-silyl-substituted-1,3-butadiene)s

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ABSTRACT: Catalytic hydrogenation of five poly(2-silyl-substituted-1,3-butadiene)s and block copolymers containing silyl functions was carried out under various conditions. The polymers were allowed to react with hydrogen at an initial pressure of 80 atm in cyclohexane at 110 °C for 5 h in the presence of palladium on carbon, leading to quantitative saturation of the double bonds regardless of the substituent on silicon atom. Molecular weights and the molar ratio of catalyst to double bonds influence the degree of hydrogenation (DH). The higher molecular weight lowers the DH. Wilkinson's complex, $Rh(PPh_3)_3Cl$, showed no activity for the hydrogenation of *cis*-1,4-poly[2-(triisopropoxysilyl)-1,3-butadiene] whereas it was effective for *cis*-1,4-polyisoprene and dangling vinyl groups in other silyl-substituted polydienes.

## Introduction

Polyolefins such as polyethylene and polypropylene are well-known commodity polymers and are used in many fields. In many cases, they are produced by free-radical polymerization or coordination polymerization with a Ziegler type catalyst. Because the polymerization mechanisms include transfer and termination reactions, polyolefins and block copolymers with polyolefin segments can have branched structures and broad distribution of molecular weights. To obtain polyolefins and the block copolymers with controlled chain structures, polydienes and the block copolymers produced by anionic living polymerization are hydrogenated under suitable conditions to be converted to polyolefins without losing their original characteristics such as molecular weight, molecular weight distribution, and microstructure. Many authors have reported the preparation of tailor-made polyolefins by this method.[1] Since the molecular weight, molecular weight distribution, and the structure of the repeating unit in the resulting polyolefins can be precisely controlled by the polymerization condition of the original 1,3-dienes, this relatively complicated synthetic method is still attractive both in academic and industrial fields. Poly(ethylene-*alt*-propylene), poly(ethylethylene), and atactic polypropylene with a narrow molecular weight distribution were synthesized[2] by hydrogenation of 1,4-polyisoprene, 1,2-polybutadiene, and poly(2-methyl-1,3-pentadiene), respectively. The solution properties of these polymers such as characteristic ratio and temperature coefficients of unperturbed dimensions were studied. Polyethylene–poly(1-butene) block copolymer derived from 1,4-polybutadiene–1,2-polybutadiene block copolymers can be used as thermoplastic elastomers.[3] When the poly[styrene-

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**Table I**
**Anionic Polymerization of 1–5[a] and the Microstructure of Resulting Polymers**

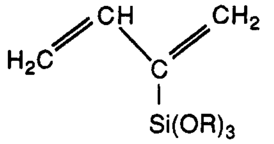
| monomer | $\bar{M}_n$(calcd)[b] | $\bar{M}_n$(obsd)[c] | $\bar{M}_w/\bar{M}_n$ | microstructure, % | | | |
|---|---|---|---|---|---|---|---|
| | | | | 1,4-*E* | 1,4-*Z* | 1,2 | 3,4 |
| 1 | 13 000 | 16 000 | 1.09 | 100 | 0 | 0 | 0 |
| | 36 000 | 31 000 | 1.11 | 100 | 0 | 0 | 0 |
| | 55 000 | 51 000 | 1.20 | 100 | 0 | 0 | 0 |
| 2 | 24 000 | 25 000 | 1.21 | 73 | 27 | 0 | 0 |
| 3 | 14 000 | 13 000 | 1.19 | 62 | 19 | 19 | 0 |
| | 28 000 | 21 000 | 1.30 | 62 | 19 | 19 | 0 |
| 4 | 17 000 | 16 000 | 1.19 | 47 | 30 | 23 | 0 |
| 5[d] | 5 900 | 8 300 | 1.29 | 67 | 11 | 13 | 9 |

[a] Polymerization was carried out in THF at -78 °C for 90–160 h. [b] Based on monomer to initiator ratio. [c] Measured by VPO in benzene at 40 °C. [d] Polymerized at 20 °C for 48 h in hexane containing 10 vol % of *N,N,N′,N′*-tetramethylethylenediamine.

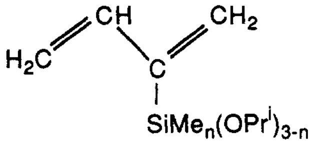
*b*-ethylene] prepared by the selective hydrogenation of poly[styrene-*b*-butadiene] is added to the blend of polystyrene and polyethylene, the block copolymer is aligned at the interface of the polymer domains.[4] A small amount of the hydrogenated block copolymer in the immiscible homopolymer mixture greatly reduces the interfacial tension and can lead to a macroscopically homogeneous polymer blend. Carboxy-terminated polyethylene, which can be used for the surface functionalization of polyethylene, was prepared by the hydrogenation of the polybutadienoic acid obtained by carboxylation of anionic living polybutadiene.[5] Deuterium-labeled polyolefins for small-angle neutron scattering studies were also obtained by the hydrogenation of polybutadienes of narrow molecular weight distributions with deuterium gas.[6]

Although many studies have been done on the hydrogenation of polydienes as mentioned above, reduction of polydienes containing alkoxysilyl functions was not reported yet. In the previous papers, we have reported the anionic polymerization of 2-(trialkoxysilyl)-1,3-butadienes, 1 and 2.[7] The anionic living polymerizations of these monomers were found to proceed under rigorously limited conditions to give homopolymers and block copolymers of controlled molecular weights and narrow molecular weight distributions. Microstructure of the resulting polymers was predominantly 1,4-*E* (cis-1,4 configuration in the polymer chain) regardless of the polymerization conditions.

The complete hydrogenation of poly(1) and poly(2) would give alternating copolymers of ethylene and vinyltrialkoxysilanes, which may be used as new polymeric silane coupling agents. In this paper, we report the catalytic hydrogenation of poly(1) and block copolymers of isoprene and 1 under various conditions. In addition, other silyl-substituted polydienes, poly(2) through poly(5), are also hydrogenated under similar conditions and the activities of catalysts toward the double-bond saturation of the polydienes with various microstructures and substituents on a silicon atom are discussed.


1 : R = Pr$^i$

2 : R = Me


3 : n = 1

4 : n = 2

5 : n = 3

## Results and Discussion

**Polymerization and Block Copolymerization of 1,3-Dienes Containing Silyl Groups.** In the previous paper, we have reported the anionic polymerization of 2-(trialkoxysilyl)-1,3-butadienes under various conditions. Since the propagating chain ends derived from these monomers are potentially deactivated by the reaction with trialkoxysilyl functions, control of the polymerization conditions is necessary to avoid such a chain termination reaction. Poly(1) and poly(2) prepared at -78 °C with potassium counterion showed narrow molecular weight distributions with desired molecular weights as described elsewhere.[7] The anionic polymerizations of 3–5 were also carried out under a similar condition unless otherwise specified.

Upon addition of the monomers, 1–4, to the THF solution of a potassium salt of oligo($\alpha$-methylstyrene), the red of the initiator changed immediately to brownish orange in all cases. This color remained unchanged at -78 °C for at least 90 h and disappeared by quenching with a small amount of methanol, resulting in quantitative yield of the polymer. The results of polymerization are shown in Table I. For each case, the observed molecular weight by vapor pressure osmometry (VPO) agrees fairly well with the calculated one based on monomer to initiator ratio. Also the molecular weight distributions are relatively narrow. The microstructures of the resulting polymers are of considerable interest since the physical properties of polydienes depend on the mode of polymerization (1,4, 1,2, or 3,4) and the geometry of the monomer unit, *E* and *Z*. For each polymer obtained in this study, the microstructure was analyzed by $^1$H and $^{13}$C NMR spectroscopies according to the assignment determined previously.[7] The results are also summarized in Table I. What we should notice here is that poly(3), poly(4), and poly(5) contained a considerable amount of 1,2-structure whereas the 1,4-mode was the exclusive structure for poly(1) and poly(2) regardless of the polymerization conditions. Although the exact reason was not clear yet, likely explanations might be the effect of steric hindrance and the electronic effect caused by the substituent on silicon atom.

Block copolymerizations were performed by addition of 1 to anionic living polyisoprene in THF at -78 °C to afford the polymers in quantitative yields. The results of block copolymerization are summarized in Table II. The block copolymers produced have very narrow molecular weight distributions, and the block lengths are close to the ones calculated from the ratio of monomer to initiator. The living nature of the polymerization reflects these well-defined chain structures in the block copolymer. However, the crossover reaction between living poly(1) and isoprene does not occur because of the lower reactivity of the poly(1)-yl radical anion as mentioned previously.[7]

**Table II**
**Anionic Block Copolymerization of 1 with Isoprene**[a]

| | $(\mathrm{Isp})_m$-$(1)_n$ | | | |
|---|---|---|---|---|
| entry | $m$ | $n$ | total $\bar{M}_n$ | $\bar{M}_w/\bar{M}_n$ |
| B-1 | 171 | 9 | 14 000 | 1.08 |
| B-2 | 317 | 33 | 30 000 | 1.04 |

[a] Polymerization was carried out in THF at −78 °C with cumylpotassium as an initiator.

**Hydrogenation of Polydienes with Alkoxysilyl Groups.** There have been many reports on a conventional polymer modification, hydrogenation.[1] The conversion of unsaturated polymers to saturated ones can be effected by both noncatalytic and catalytic methods. Each of these techniques has unique characters, and the suitable method should be chosen for the yield, selectivity, side reactions, and/or catalyst poisoning and removal. A typical noncatalytic method such as diimide reduction has an advantage with its high reactivity and ease of handling. However, it is necessary to use an equimolar or more amount of hydride reducing agents and therefore disfavored from the economical aspect. Moreover, labile diimide is usually generated by oxidation of hydrazine in aqueous solution or by thermal decomposition of *N*-*p*-toluenesulfonohydrazide. Under these reaction conditions, polydienes containing alkoxysilyl groups are easily hydrolyzed, resulting in cross-linking of a polymer chain. On the other hand, catalytic hydrogenation is a simple and economical process because molecular hydrogen can be used as a hydride donor. Although typical transition-metal catalysts such as Wilkinson's catalyst and palladium on carbon (Pd/C) have high activity, it might be deactivated by a small amount of catalyst poisons, such as the ligands of a Ziegler catalyst, additives for initiation, and regulation of molecular weight. Therefore the starting polydienes should be purified.

**Hydrogenation of Polydienes with Pd/C.** Among various types of heterogeneous catalysts, palladium-based systems are well-known and are often used in organic synthesis for their high activity and selectivity.[8] Applications of this catalyst to the hydrogenation of polydienes were reported by several workers. Pd/$CaCO_3$ was used for the hydrogenation of 1,4-polybutadiene,[9] 1,2-polybutadiene,[10] and 1,4-polyisoprene[11] to prepare the well-defined polyolefins whose solution properties can be investigated in relation with the primary structure. Zotteri and Giuliani used Pd/C for the reduction of poly(styrene-*b*-isoprene-*b*-styrene) to poly[vinylcyclohexane-*b*-(ethylene-*alt*-propylene)-*b*-vinylcyclohexane], the elastomeric behavior of which was studied.[12] Conversions were 100% in all of these cases. The hydrogenation of aromatic rings in the block copolymer indicates the high activity of the palladium catalyst whereas Wilkinson's catalyst does not work. As can be seen from these results, the palladium catalyst was effective for the hydrogenation of double bonds in polymers as well as in low molecular weight compounds. Accordingly, we chose Pd/C as a catalyst for the hydrogenation of polydienes with silyl functions.

The polymers in cyclohexane were hydrogenated in the presence of Pd/C in an autoclave with continuous magnetic stirring. After removal of the catalyst and solvent, the hydrogenated polymer was analyzed by FT-IR, $^1$H NMR spectroscopies, and gel permeation chromatography (GPC).

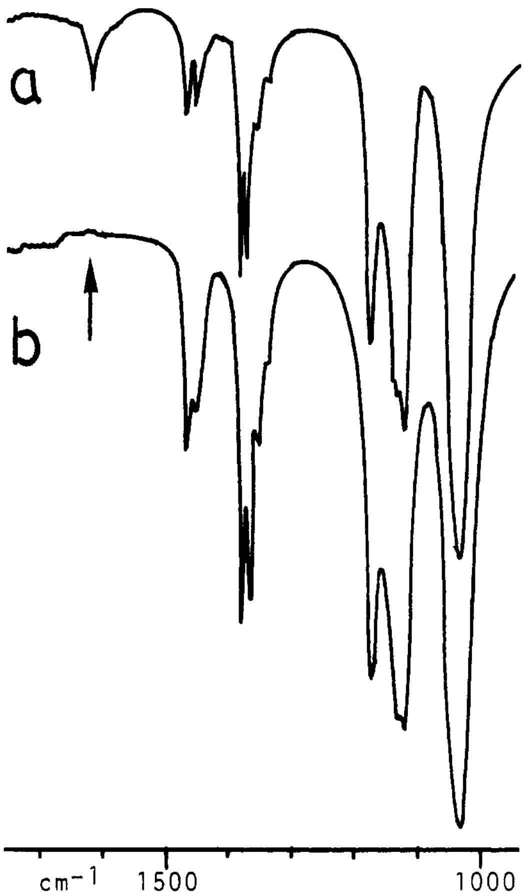


**Figure 1.** Expanded IR spectra of (a) poly(1) and (b) a hydrogenated one.

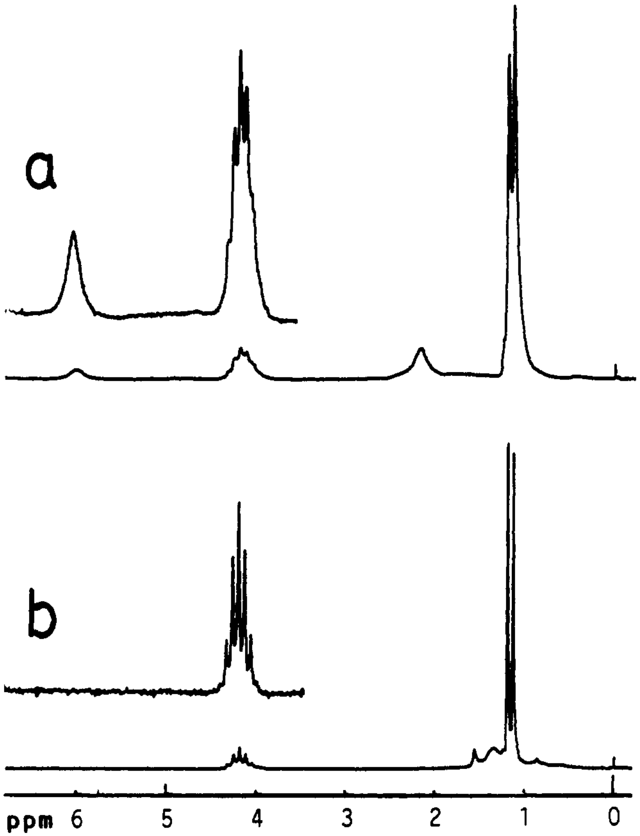


**Figure 2.** 90-MHz $^1$H NMR spectra of (a) poly(1) and (b) a hydrogenated one recorded in $CDCl_3$ at 50 °C.

Figures 1 and 2 show typical IR and $^1$H NMR spectra of poly(1) and the hydrogenated one, respectively. As was mentioned before,[7] poly(1) has 100% 1,4-*E* linkage, which is proved by the corresponding IR absorption bands and resonance signals observed in the spectra. In the IR spectrum, absorption at 1614 cm$^{-1}$ due to the stretching vibration of the carbon–carbon double bond in the main

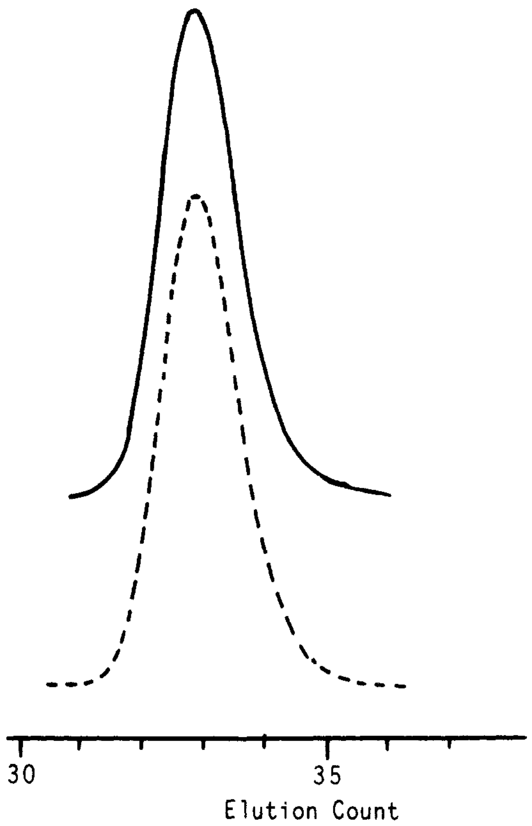


**Figure 3.** GPC traces of poly(1) and a hydrogenated one: (—) before hydrogenation; (- - -) after hydrogenation.

chain diminished after hydrogenation. The stretching absorption band of the Si–H bond, which might be formed by the reduction of alkoxysilyl function, was not observed in the region of 2280–2050 cm$^{-1}$.[13] In the $^1$H NMR spectrum, the signals at 6.1 and 2.1 ppm attributable to the olefinic proton and methylene protons adjacent to the vinyl group disappear completely. The degree of hydrogenation (DH) was determined by the relative integrated intensities of olefinic protons and those of alkyl protons attached to silyl groups. The heptet splitting for the methyne proton (4.2 ppm) of the isopropyl group became clear by hydrogenation, indicating the increased mobility of the silyl group attached to the main chain. Figure 3 shows GPC traces of poly(1) and the hydrogenated one. As can be seen, the molecular weight distribution (MWD) was very narrow and unchanged after hydrogenation, supporting that neither main-chain scission nor branching occurred during the reaction and workup process.

The result of hydrogenation catalyzed with Pd/C is summarized in Table III. The DH values are measured by $^1$H NMR for each microstructure. As can be seen, the higher the molecular weight of the polymer, the lower DH becomes (entries 1-1, 1-3, 3-1, 3-2). When large amounts of catalyst were used, significant improvement was observed regardless of the substituent on the silicon atom, the molecular weight, and the microstructure (entries 1-2, 1-4, 1-8, 2-2, 3-3, 3-5, 4-2). In polymer reactions, the rate is occasionally affected by the diffusion of substrate in solution. The effect of molecular weights and the catalyst concentration on conversion can be explained by the low mobility of the polymer chain toward the heterogeneous catalyst site. In addition, the rate of coordination of the double bond to the catalyst might also be lowered on account of the bulky polymer chain.

The effect of the microstructure on DH was obvious. In the catalytic hydrogenation of low molecular weight olefins, generally, the terminal double bond was hydrogenated faster than the inner one presumably due to the steric hindrance about the double bond. A similar tendency is observed in this study. Although poly(1) and poly(2) consist of exclusive 1,4-linkages, a considerable amount of 1,2-structure was contained in poly(3), poly(4), and poly(5), where the dangling vinyl groups were hydrogenated faster than the double bond in the polymer chain (entries 3-2, 3-3, 4-2, 4-3, 5-1).

**Hydrogenation of Polydienes with $Rh(PPh_3)_3Cl$.** $Rh(PPh_3)_3Cl$, commonly known as Wilkinson's catalyst, is often used in organic synthesis because of its solubility in organic solvents and high activity for the hydrogenation of alkenes.[14] It catalyzes the hydrogenation of low molecular weight alkenes under mild conditions, even at ambient temperature and pressure. Many authors have reported that this catalyst is also effective for the hydrogenation of unsaturated high molecular weight polymers. Doi et al. used this catalyst to hydrogenate polybutadienes of various molecular weight and microstructures.[15] The relative reactivity of the double bond is demonstrated to be 1,2- > cis-1,4- > trans-1,4- in decreasing order. Gilliom used Wilkinson's catalyst for the hydrogenation of syndiotactic 1,2-polybutadiene and SBS type block copolymer in the absence of solvent.[16] In spite of the slow reaction rate, high conversion (>90%) can be obtained at moderate temperature and pressure. It was concluded that a reducible polymer domain was kept mobile on the molecular level and dissolved the catalyst throughout the reaction since the hydrogenation was performed at a temperature higher than the $T_g$s of the polymer matrix resulting in the large turnover numbers (>1000). The relative reactivity was syndiotactic 1,2-polybutadiene > midblock of SBS where the polybutadiene segment consisted of 85% 1,4-linkage. This is consistent with Doi's results.

In general, soluble homogeneous catalysts such as Wilkinson's catalyst have higher chemoselectivity than heterogeneous catalysts. Palladium catalyst hydrogenates unsaturated nitrile compounds to unsaturated amines if the carbon–carbon double bonds were sterically hindered.[17] With Wilkinson's catalyst, carbon–carbon double bonds in the polymer containing functional groups such as butadiene–acrylonitrile copolymer,[18] a carboxy-terminated polybutadiene,[19] were selectively hydrogenated without affecting the functional groups.

The hydrogenation with $Rh(PPh_3)_3Cl$ was carried out in the same manner as described for a palladium-catalyzed reaction except for the use of toluene instead of cyclohexane. After reaction, the yellow homogeneous reaction mixture was poured into a large excess of methanol, and the hydrogenated polymer was isolated as precipitate. The results of hydrogenation with $Rh(PPh_3)_3Cl$ are summarized in Table IV. Unexpectedly, no hydrogenation took place for poly(1) although the high activity of the catalyst was confirmed by the hydrogenation of *cis*-1,4-polyisoprene with a molecular weight of 2 × 10$^6$ under the same condition to give an alternating copolymer of ethylene and propylene. Furthermore, the same reaction was carried out in the presence of poly(1), resulting in quantitatively hydrogenated polyisoprene and unreacted poly(1). This indicates that the inertness of poly(1) to rhodium-catalyzed hydrogenation was caused not by catalyst poisoning but by, presumably, steric hindrance about the double bond of the 1,4-*E* linkage. Partial hydrogenation of the 1,4-linkage in poly(2), poly(3), poly(4), and poly(5) may occur at the 1,4-*Z* double bond. The complete hydrogenation of the dangling vinyl group in

**Table III**
**Catalytic Hydrogenation of Poly(1) through Poly(5) with Pd/C[a]**

| | | | | | | DH (%)/microstructure (%)[b] | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| polymer | entry | $\bar{M}_n$(obsd) | $H_2$, atm | Pd/C=C, mol % | time, h | 1,4-*E* | 1,4-*Z* | 1,2 | 3,4 | total |
| poly(1) | 1-1 | 16 000 | 25 | 10 | 5 | 82/100 | - | - | - | 82 |
| | 1-2 | | 80 | 30 | 90 | 100/100 | - | - | - | 100 |
| | 1-3 | 31 000 | 25 | 10 | 5 | 25/100 | - | - | - | 25 |
| | 1-4 | | 80 | 30 | 93 | 100/100 | - | - | - | 100 |
| | 1-5 | 51 000 | 25 | 10 | 44 | 52/100 | - | - | - | 52 |
| | 1-6 | | 80 | 25 | 5 | 84/100 | - | - | - | 84 |
| | 1-7 | | 80 | 10 | 44 | 54/100 | - | - | - | 54 |
| | 1-8 | | 80 | 30 | 90 | 95/100 | - | - | - | 95 |
| poly(2) | 2-1 | 25 000 | 25 | 30 | 5 | 54/73 | 25/27 | - | - | 79 |
| | 2-2 | | 80 | 25 | 91 | 73/73 | 27/27 | - | - | 100 |
| poly(3) | 3-1 | 13 000 | 25 | 10 | 5 | 37/62 | 14/19 | 10/19 | - | 61 |
| | 3-2 | 21 000 | 25 | 10 | 5 | 25/62 | 10/20 | 10/18 | - | 45 |
| | 3-3 | | 80 | 30 | 12 | 70/82 | | 18/18 | - | 88 |
| | 3-4 | 16 000 | 25 | 10 | 5 | 37/94 | | 4/6 | - | 41 |
| | 3-5 | | 25 | 30 | 5 | 84/94 | | 6/6 | - | 90 |
| poly(4) | 4-1 | 16 000 | 25 | 10 | 5 | 15/47 | 12/30 | 12/23 | - | 39 |
| | 4-2 | | 25 | 30 | 5 | 65/77 | | 23/23 | - | 88 |
| | 4-3 | | 80 | 10 | 12 | 58/77 | | 23/23 | - | 81 |
| poly(5) | 5-1 | 8 300 | 25 | 10 | 5 | 46/78 | | 9/13 | 5/9 | 60 |
| | 5-2 | | 80 | 10 | 12 | 69/78 | | 9/13 | 7/9 | 85 |

[a] Carried out in autoclave at 110 °C in cyclohexane. [b] Denominator and numerator are numbers of carbon–carbon double bonds and the hydrogenated one in each microstructure out of 100 repeating units. A dash indicates that the corresponding structure was not observed in the original polydienes.

**Table IV**
**Catalytic Hydrogenation of Poly(1) through Poly(5) with $Rh(PPh_3)_3Cl$[a]**

| | | | | | | DH (%)/microstructure (%)[b] | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| polymer | entry | $\bar{M}_n$(obsd) | $H_2$, atm | Rh/C=C, mol % | time, h | 1,4-*E* | 1,4-*Z* | 1,2 | 3,4 | total |
| poly(1) | 1-9 | 14 000 | 50 | 2 | 42 | 0/100 | - | - | - | 0 |
| poly(2) | 2-3 | 25 000 | 50 | 2 | 200 | 11/100 | | - | - | 11 |
| poly(3) | 3-6 | 13 000 | 50 | 2 | 90 | 11/88 | | 18/18 | - | 29 |
| poly(4) | 4-4 | 16 000 | 50 | 2 | 90 | 8/77 | | 23/23 | - | 31 |
| poly(5) | 5-3 | 8 300 | 50 | 2 | 90 | 16/78 | | 13/13 | 9/9 | 35 |

[a] Carried out in an autoclave at 100 °C in toluene. [b] Denominator and numerator are numbers of carbon–carbon double bonds and the hydrogenated one in each microstructure out of 100 repeating units. A dash indicates that the corresponding structure was not observed in the original polydienes.

**Table V**
**Catalytic Hydrogenation of Poly(isoprene-*b*-1)**

| | | | | | degree of hydrogenation | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | catalyst | | | polyisoprene | | | | poly(1) |
| entry | $H_2$, atm | type | mol % | time, h | 1,2 | 3,4 | 1,4-*E* | total | 1,4-*E* |
| B-1-1 | 80 | Pd | 3.6 | 64 | 22/22 | 58/58 | 17/17 | 100/100 | 100/100 |
| B-2-1 | 80 | | 5.3 | 64 | 33/33 | 50/57 | 10/10 | 93/100 | 100/100 |
| B-1-2 | 50 | Rh | 1.1 | 46 | 22/22 | 58/58 | 3/17 | 83/100 | 0/100 |
| B-2-2 | 50 | | 0.38 | 88 | 33/33 | 57/57 | 2/10 | 92/100 | 0/100 |

these polymers can be explained by the ease of coordination of double bond to the catalyst.

**Hydrogenation of Block Copolymers.** Synthesis of block copolymers, which can lead to heterophase materials, has stimulated a great deal of interest. Hydrogenated SBS and SIS types of block copolymer where S, B, and I represent polystyrene, polybutadiene, and polyisoprene segments, respectively, are commercially produced as a thermoplastic elastomer.[20] The hydrogenated SB type block copolymer is used as a surfactant in the field of polymer alloys.[4] In the previous paper, we have described the synthesis of block copolymer with polyisoprene and poly(1) segments by sequential anionic polymerization.[7] Hydrogenation of the block copolymer is expected to lead a unique one containing polyolefin segments with and without alkoxysilyl function.

The results of hydrogenation of poly(isoprene-*b*-1) are summarized in Table V. Since the block copolymerization was carried out in THF with a potassium counterion, the microstructure of the polyisoprene segment was a mixture of 1,4-*E*-, 1,2-, and 3,4-adducts. With a Pd/C catalyst, both of the segments were almost hydrogenated. Figure 4 shows GPC traces of the block copolymer and the hydrogenated one. The hydrogenated block copolymer has a very narrow molecular weight distribution curve, which slightly shifted to the lower molecular weight side from that of the original polymer. This indicates that neither chain scission nor cross-linking of the polymer chain occurred during the hydrogenation reaction. The small difference of apparent molecular weight was presumably due to the change of hydrodynamic volume of the polymer chain. Parts a and b of Figure 5 show $^1H$ NMR spectra of the block copolymer and the hydrogenated one, respectively. As can be seen, signals attributable to olefinic protons disappeared completely and intensities of the signals due to methyl and methylene protons increased. When $Rh(PPh_3)_3Cl$ was used as a catalyst, selective hydrogenation of the polyisoprene segment occurred. Dangling vinyl groups of 1,2- and 3,4-structures in the polyisoprene segment were completely hydrogenated whereas the poly(1) segment was kept

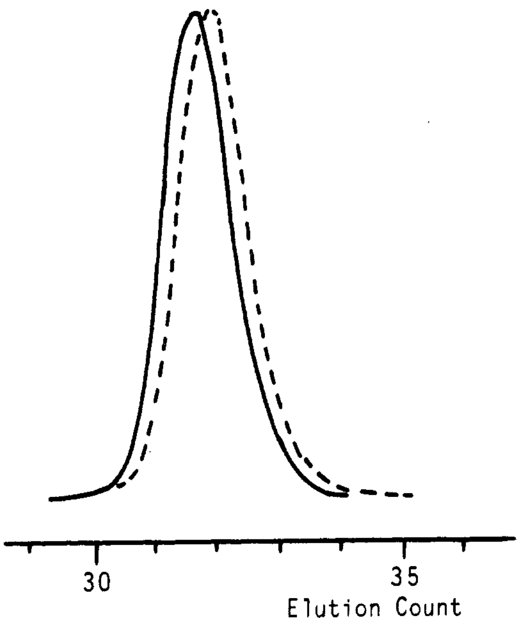


**Figure 4.** GPC traces of poly(isoprene-*b*-1) and a hydrogenated one: (—) before hydrogenation; (- - -) after hydrogenation.

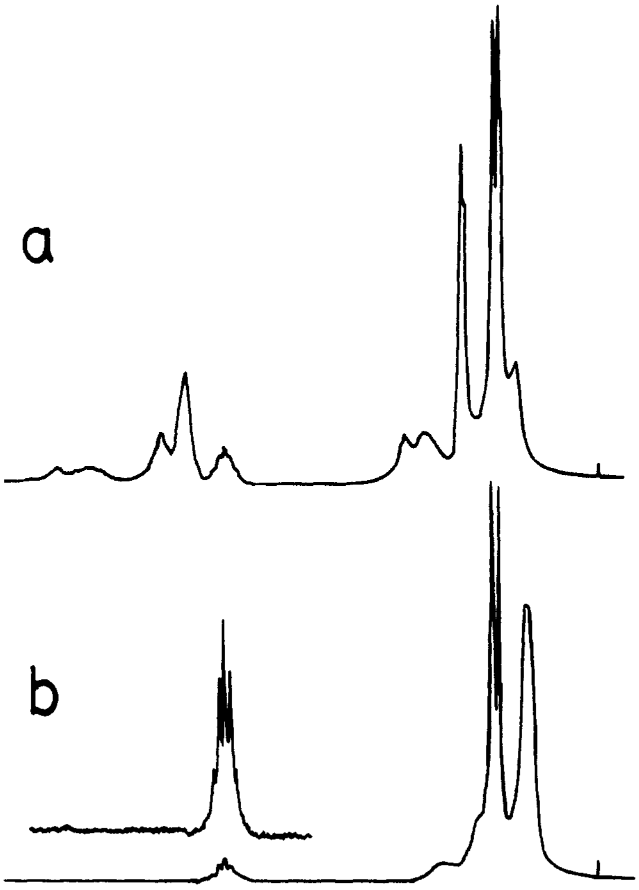


**Figure 5.** 90-MHz $^1H$ NMR spectra of (a) poly(isoprene-*b*-1) and (b) a hydrogenated one recorded in $CDCl_3$ at 50 °C.

unchanged. This agrees well with the results of the hydrogenation of polyisoprene in the presence of poly(1) as mentioned above.

In addition, the effect of microstructure on the degree of hydrogenation of the polyisoprene segment was obvious compared with that in palladium-catalyzed hydrogenation. The low reactivity of the 1,4-*E* double bond of the polyisoprene segment could be explained by the difficulty of coordination of the double bond to the catalyst surface.

## Experimental Section

**Materials.** Poly(1) through poly(5) and block copolymers containing a poly(1) segment were prepared by anionic polymerization under high-vacuum conditions ($\sim 10^{-6}$ mmHg) using cumylpotassium or butyllithium as an initiator. After the completion of the polymerization, the reaction mixture was poured into a large excess of water to precipitate the polymers. Then it was extracted three times with ether, and the combined organic layer was dried over anhydrous $MgSO_4$. The polymer obtained was purified by reprecipitation two additional times from THF/methanol and dried in vacuo. Synthetic *cis*-1,4-polyisoprene (IR2000, Japan Synthetic Rubber, $\bar{M}_n \approx 2 \times 10^6$ estimated by GPC) was used without further purification. Palladium on carbon (10% on activated carbon, Aldrich) and $Rh(PPh_3)_3Cl$ (Merck) were used as received. Cyclohexane and toluene were purified according to the well-known procedure.

**Hydrogenation Procedure.** A typical hydrogenation procedure is as follows. About 100 mg of polydiene was weighed in a glass vessel and was dissolved in 10 mL of dry cyclohexane (for Pd/C) or in toluene (for Wilkinson's catalyst), which was degassed by bubbling dry nitrogen gas just prior to use. An appropriate amount of catalyst (40–100 mg of Pd/C and/or 7–15 mg of Wilkinson's catalyst) was added to the reaction mixture. The accurate amount of catalyst should be used according to the type of polydienes and the molar ratio to double bonds. (See Tables III–V.) Then it was transferred into an autoclave, and the pressure-resistant reactor was purged with hydrogen gas by at least four cycles of a pressurize–depressurize technique and kept at 100–110 °C for 90 h in an oil bath. After the completion of the reaction, the hydrogenated polymer was isolated by filtration followed by evaporation (for Pd/C) or reprecipitation with methanol (for Wilkinson's catalyst). This experimental scale was chosen for ease of handling of the limited amount of silyl-substituted polydienes precursors. It was possible to hydrogenate larger amounts of materials ($\sim$1 g).

**Polymer Analysis.** $^1H$ NMR measurement was run on a JEOL FX-90Q instrument at 89.60 MHz with the Fourier transform mode. The spectra were recorded at 50 °C with 5 wt % of $CDCl_3$ solution charged in a 5-mm sample tube, 8192 data points, 900-Hz spectral width, a 45° pulse, and a repetition of 5.0 s. FT-IR spectra of polymer sample cast from benzene solution on KRS-5 disk were recorded with an Analect AQS-20M instrument. Gel permeation chromatography (GPC) was measured by using a Toso HLC-8020 instrument at 40 °C with differential refractive index detection, THF being the elution solvent at a flow rate of 0.8 mL/min. The number-average molecular weights were measured by vapor pressure osmometry (VPO) by using a CORONA 117 instrument at 40 °C in benzene solution. Under very precise temperature control with thermocouples with high sensitivity, a molecular weight up to 1 × $10^5$ could be determined within an analytical error of ±10%, which was confirmed by measuring the molecular weight of polystyrene standard samples.

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**Registry No.** 1 (homopolymer), 104955-52-4; (1)(isoprene) (block copolymer), 117861-50-4; 2 (homopolymer), 104955-47-7; 3 (homopolymer), 126726-58-7; 4 (homopolymer), 113177-19-8; 5 (homopolymer), 116767-56-7.

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# A Statistical Theory of Globular Polyelectrolyte Complexes

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ABSTRACT: A microscopic statistical theory of a symmetrical polyelectrolyte complex (PEC) is developed. PEC is shown to form a polymer globule. The equilibrium density of PEC, the width of a PEC surface layer, and the surface tension of PEC are calculated as a function of salt concentration. Description of PEC as a polymer globule enables us to simplify theoretical treatment of the phenomenon of phase separation in polyelectrolyte solutions (complex coacervation). Numerous experimental facts concerning complex coacervation are easily explained within this approach. Complex coacervation is considered as precipitation of polymer globules owing to minimization of surface energy. The theory is based on the Lifshitz–Grosberg theory of polymer globules and our previous work concerning the equation of state of polyelectrolyte solutions. It is limited to the case of polyions with the low linear density of charge, which is most clear from the theoretical point of view and is also of practical and, in particular, of biological interest.

## I. Introduction

It is well-known that oppositely charged macromolecules in a solution form polyelectrolyte complexes (PEC). Their theoretical investigation is important for the development of a theory of phase separation in a polyelectrolyte (PE) system containing polyions of opposite charges. This phenomenon studied for the first time by Bungenberg de Jong[1] was called complex coacervation (see also refs 2–4). Parts of the condensed phase (coacervate) are usually called coacervate drops and are often considered as model systems for precellular structures.[5] The numerous phenomena that occur in the PE solutions are complicated, and generally their theoretical interpretation is qualitative and controversial. Therefore, it is reasonable to start the consistent consideration of these systems with the most simple solvable model, where main qualitative features are already seen.

As the first step in the study of PEC properties we shall consider in this paper a symmetric PEC, formed by two flexible oppositely charged polyions with the same degree of polymerization $N$ and each having one charge per $m$ monomers (each polyion has charges of one sign). Charges should be distributed more or less uniformly along the chain (for example, randomly). Only for simplicity we consider polyions as flexible filaments on which interacting monomers are strung (the model "beads on a filament"[6]) with Gaussian correlations between adjacent monomers and the mean-square distance, $a^2$, between them. All the monomers interact by means of non-Coulombic forces of the van der Waals type. These assumptions are typical for the theoretical consideration of this kind[2–4] and can be easily generalized.

The influence of ionic bonds between oppositely charged monomers is supposed to be small (for example, the energy of an ionic bond is small in comparison with temperature $T$, given in energy units). Thus PEC is formed, owing to fluctuation electrostatic energy. This energy was calculated in ref 7 for polyelectrolyte solution (PES) containing weakly charged macromolecules. (Polyions are called weakly charged when the parameter $u/m^{1/2}$ is small, where $u = l/a$, $l = e^2/\epsilon T$ is the Bjerrum length (see also ref 8), and $\epsilon$ is the dielectric constant of the solvent. It was also shown[7] that Coulombic and nonelectrostatic contributions to the free energy may be of the same order of magnitude, which can lead to PEC formation. Weakly charged PE are of

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