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Studies on Nickel-Containing Ziegler-Type Catalysts. II. Low Molecular Weight (Liquid) Poly(diene)s with 1,4-Microstructure

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Liquid polybutadiene and liquid polyisoprene, which are usefull precursor for coatings, plastisizers or lubricants, were effectively synthesized by polymerizing butadiene and isoprene, respectively, in the presense of a nickel-containing Ziegler-type catalyst utilizing a lower α-olefin or molecular hydrogen as a molecular weight regulator. The catalyst consists of four components; nickel naphthenate ($Ni(naph)_2$)/$AlEt_3$/(trichloromethyl)benzene(BTC)/triphenyl phosphite (TPP) or triphenylphosphine (TPN). The microstructure of these liquid polymers is mainly 1,4-(*cis*/*trans*), which is advantageous for their reactivity and the rheological properties. The hydrogenated low molecular weight liquid polyisoprene exhibited very similar properties to those of squalane, which is a hydrogenated product of natural squalene.

In spite of their usefulness of luquid poly(diene)s, there has been no report concerning details of their synthesis. In a preceding paper,[1] we reported that when being combined with a fluorine atom and a Lewis acidic component, the nickel-containing Ziegler-type catalyst exhibits excellent properties for the polymerization of butadiene to a high *cis*-1,4 microstructure with a high molecular weight.

In this paper we report that our nickel catalyst can catalyze the 1,4-(*cis*/*trans*) polymerization of diolefins (butadiene or isoprene) to low molecular weight when being combined with chlorine atoms and electron donative ligands, such as phosphines or phosphites. Furthermore, lower α-olefin or molecular hydrogen was found to be an efficient molecular weight regulator. It is also reported that an alternative of natural squalane is obtainable by the hydrogenation of low molecular weight liquid polyisoprene.

Experimental

Materials. 1,3-Butadiene (C_4'') and toluene (solvent) were purified as described in our preceding paper.[1] Isoprene (C_5'') and (trichloromethyl)benzene (BTC) were dried over molecular sieve (3A), and purified by distillation. Propylene (C_3') was evaporated from the container and cold-trapped over the molecular sieve (3A). Hydrogen was used directly from the container. $AlEt_3$ and $AlEt_{1.5}Cl_{1.5}$ were used as obtained. Other catalyst components, such as nickel naphthenate ($Ni(naph)_2$), triphenyl phosphite (TPP) and triphenylphosphine (TPN), were of extra pure chemical grade, and were used as obtained.

Experimental Procedure and Analysis. Catalyst preparation and polymerization were conducted similarly as described in our preceding paper.[1] The microstructure of the polymer was analyzed by IR spectroscopy and calculated using D. Morero's method.[2] The viscosity (η) was measured with an E-type rotary viscometer at 20 °C. The average molecular weight of the polymer was measured with a vapor-pressure osmometer using benzene as the solvent at 20 °C.

Results and Discussion

Liquid Polybutadiene. Influences of electron-donative ligands on the $Ni(naph)_2$/$AlEt_3$/(trichloromethyl)benzene(BTC) catalyst. It has been known that a nickel catalyst combined with organoaluminum chloride affords liquid polybutadiene with a 1,4-(*cis*/*trans*) microstructure. From the industrial point of view, however, the molecular weight and viscosity of liquid polybutadiene are not sufficiently low, especially at higher monomer concentrations. We therefore investigated how to effectively lower the molecular weight by modifying the nickel catalyst. Instead of organoaluminum chloride, (trichloromethyl)benzene was selected as the chlorine source for $AlEt_3$; by varying the molar ratio of BTC/$AlEt_3$, the chlorine content in $AlEt_{3-n}Cl_n$ can be controlled freely, as shown below:

$$AlEt_3 + (n/3)C_6H_5CCl_3 \longrightarrow AlEt_{3-n}Cl_n + (n/3)C_6H_5CEt_3. \tag{1}$$

Thus, the basic composition of our nickel catalyst can be represented by

$$Ni(naph)_2/AlEt_3/BTC. \tag{2}$$

Among the various additives examined, electron-donative ligands, such as phosphines, phosphites, phosphates, ethers and thioethers, effectively lowered the molecular weight of liquid polybutadiene (Table 1). These results are in sharp contrast to those regarding the catalyst used for high molecular weight polybutadiene,[1] in which electron-attractive additives effectively increases the molecular weight. These results indicate that the high electron density on Ni atoms promotes the chain-transfer reaction of the catalyst.

Influences of Lower α-Olefin on the $Ni(naph)_2$/$AlEt_3$/BTC Catalyst. A lower α-olefin, such as ethylene or

Table 1. Molecular Weight Control of Liquid Polybutadiene[a)]

No.	Additives		Polymer yield/%	η/cp
	Compound	Amount[b)]		
1	—	—	89.9	3000
2	Furan	0.5	85.5	963
3	Thiophene	0.2	92.7	883
4	Epichlorohydrin	0.2	62.4	739
5	Tributylphosphine	0.1	50.0	1650
6	Trimethylphosphate	0.1	65.5	970
7	Triethylphosphite	0.1	54.8	1020
8	Tridecylphosphite	0.1	88.0	750

a) Catalyst; $Ni(naph)_2(1)/AlEt_3(10)/BTC(5)/Additive$; ( ) molar ratio. Solvent; Toluene, Polymerization; 40 °C, 3 h. b) Molar ratio to $AlEt_3$.

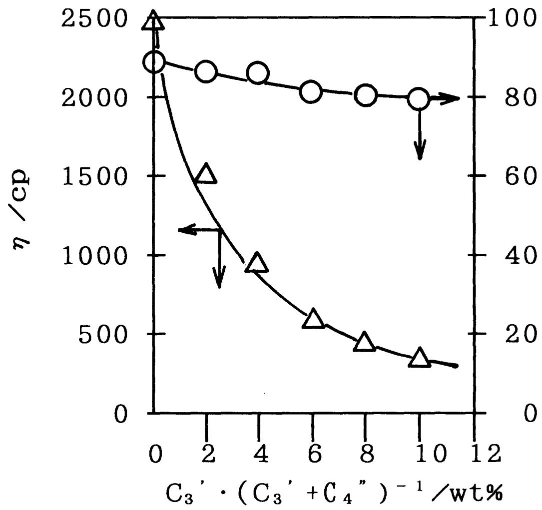


Fig. 1. Influences of C_3' on the polymerization of C_4''. ○; Polymer yield/%, △; η/cp. Catalyst; $Ni(naph)_2/AlEt_3/BTC/TPP=1/10/5/1$ (molar ratio). Polymerization; $Ni/C_4''=1.02\times10^{-4}$ (molar ratio), 40 °C, 4 h, solvent=toluene.

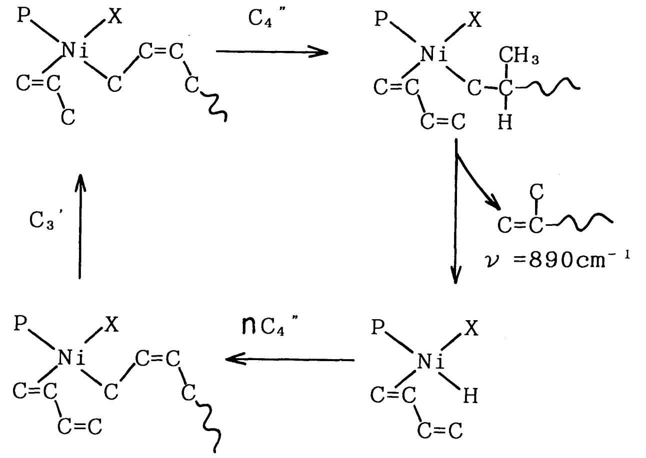


Fig. 2. Estimated mechanism of molecular weight regulation by C_3' via β-hydride elimination.

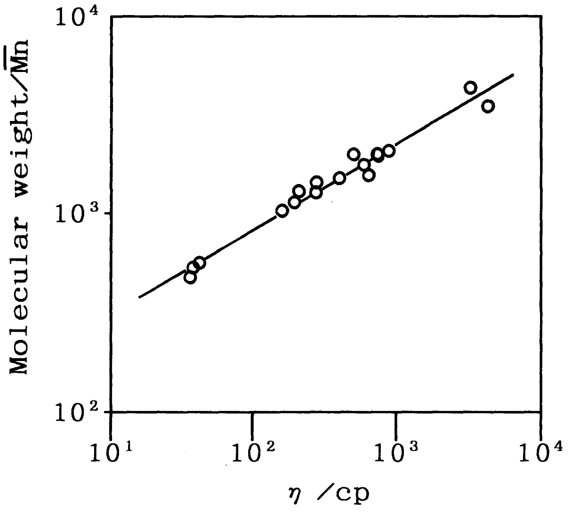


Fig. 3. Relation between the molecular weight (M_n) and viscosity of liquid polybutadiene.

propylene (C_3'), was found to be an extremely efficient molecular weight regulator in the polymerization of dienes by a nickel catalyst. Furthermore, being combined with an electron-donative ligand, such as triphenyl phosphite, the molecular weight lowering effect of the α-olefin was further promoted. A typical example for C_3' is illustrated in Fig. 1. With an increase in the C_3' content from 0 to 10%, the molecular weight of liquid polybutadiene (expressed as viscosity η) decreases rapidly. Since the yield of the polymer is kept almost constant during such an increase of the C_3' content, C_3' mainly acts as a genuin chain-transfer reagent, which regenerates active catalytic species along with the chain-transfer reaction. An IR analysis of liquid polybutadiene with very low molecular weight (the degree of polymerization $(n)\fallingdotseq10$) clearly showed the vinylidene absorption band at 890 cm^{-1}, which originated from the terminal propylene unit. Therefore, the chain-transfer mechanism by the α-olefin is interpreted as being the β-hydride elimination from a square-planer nickel complex to regenerate an active nickel hydride species, such as that illustrated in Fig. 2.

The relation between the number-average molecular weight (M_n) and the viscosity of the liquid polybutadiene was measured, and is illustrated in Fig. 3. The following empirical relation was obtained:

$$M_n = 1.267 \times 10^2 \ \eta^{0.413}. \tag{3}$$

Table 2. Typical Properties of Liquid Polybutadiene

No.	η	M_n a)	P b)	Microstructure/%		
	cp			*cis*-1,4-	*trans*-1,4-	1,2-
1	3000	3400	63	83.5	15.7	0.8
2	750	1900	35	76.2	22.6	1.2
3	100	850	16	72.0	22.0	6.0

a) Number-average molecular weight. b) Number-average degree of polymerization.

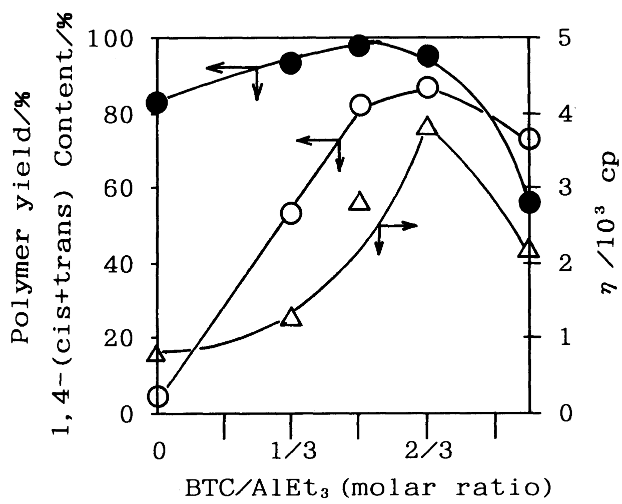


Fig. 4. Influences of (trichloromethyl)benzene (BTC) on the nickel catalyst. ○; Polymer yield/%, ●; 1,4-(*cis*/*trans*) content/% △; η/cp. Catalyst; Ni(naph)$_2$/AlEt$_3$/BTC/TPP=1/10/variable/1 (molar ratio). Polymerization; Ni/C$_4''$=1.02×10^{-4} (molar ratio), 40 °C, 4 h, solvent=toluene.

The typical properties of the liquid polybutadiene are summarized in Table 2. The content of 1,4-(*cis*/*trans*) microstructure is high as 94% at η=100 cp till 99% at η=3,000 cp (1 cp=10^{-3} Pa s).

Influences of BTC/AlEt$_3$ Molar Ratio. To determine the role of (trichloromethyl)benzene in the Ni(naph)$_2$/AlEt$_3$/BTC catalyst, the influence of the BTC/AlEt$_3$ molar ratio was examined; the results are given in Fig. 4. With an increase in the BTC/AlEt$_3$ molar ratio, both the catalytic activity and η increase. At BTC/AlEt$_3$=1, although the obtained liquid polybutadiene no longer shows any selectivity for 1,4-(*cis*/*trans*) microstructure, its microstructure is a mixture of the 1,4- and 1,2-structures. It is preferable to obtain a high activity with both low viscosity and high content of the 1,4-structure. Therefore, the optimum BTC/AlEt$_3$ ratio is 0.5, which corresponds to the composition of AlEt$_{1.5}$Cl$_{1.5}$. Actually, by using AlEt$_{1.5}$Cl$_{1.5}$ as an organoaluminum component instead of AlEt$_3$+BTC, very similar results were obtained.

Liquid Polyisoprene. Influences of the lower α-olefin and H$_2$ on the Ni(naph)$_2$/AlEt$_3$/BTC/TPN catalyst. In the case of liquid polyisoprene also, a lower α-olefin works well as a molecular weight regulator for the nickel catalyst. The results are given in Table 3. With an increase in the content of C$_3'$, the viscosity of liquid polyisoprene decreases exponetially, while the content of the 1,4-structure gradually decreases from 88.5 to 76%.

Furthermore, molecular hydrogen was found to be an efficient molecular weight regulator. Table 4 summarizes the influence of the partical pressure of H$_2$ (P_{H2}) on the Ni(naph)$_2$/AlEt$_3$/BTC/TPN catalyst. Without hydrogen, gellation takes place and no liquid

Table 3. Molecular Weight Control of Liquid Polyisoprene by Propylene (C$_3'$)$^{a)}$

No.	C$_3'$	Polymer yield/%	η	Microstructure/% b)			
	wt%		cp	*cis*-1,4-	*trans*-1,4-	1,2-	3,4-
1	6.2	61.3	10057	66.0	22.5	1.7	9.8
2	11.1	67.6	2599	59.2	26.3	1.3	13.2
3	16.3	71.0	107	53.0	26.4	2.9	17.7
4	23.4	70.0	29	48.8	32.3	3.2	15.8
5	31.3	54.5	11	47.6	28.5	4.0	20.0

a) Catalyst; Ni(naph)$_2$(1)/AlEt$_3$(10)/BTC(5)/TPN(1) ( ); molar ratio. Ni(naph)$_2$/isoprene=1.82×10^{-4} (molar ratio), Polymerization=60 °C, 8 h. b) By Binder's method.[3]

Table 4. Molecular Weight Control of Liquid Polyisoprene by H$_2$ (**1**)$^{a)}$

No.	P_{H2}	Polymer yield/%	η	M_n	Microstructure/% b)			
	atm		cp		*cis*-1,4-	*trans*-1,4-	1,2-	3,4-
1	—	—	Gelation		—	—	—	—
2	10	95.6	830	1720	60.5	21.4	1.5	16.6
3	45	85.3	28.5	375	53.5	30.8	0.9	14.8
4	80	62.4	5.7	180	52.0	30.4	2.0	15.6

a) Catalyst; Ni(naph)$_2$(1)/AlEt$_3$(10)/BTC(5)/TPN(1) ( ); molar ratio. Ni(naph)$_2$/isoprene=3.47×10^{-4} (molar ratio), Polymerization=60 °C, 12 h. b) At 30 °C. c) By Binder's method.[3]

polymer is obtained. With an increase in P_{H2} from 10 to 80 atm, both η and M_n decrease rapidly until an isoprene oligomer with a monomer unit of 2.5 to 3.0 is obtained. In this case, the content of 1,4-structure is kept at around 82%. The mechanism of molecular weight regulation by H_2 is interpreted as being hydrogenolysis of the polymer terminal coordinating to the squre-planer nickel complex (Fig. 5). At the same time, the active species, nickel hydride, is regenerated by this type of hydrogenolysis.

The influence of phosphines and phosphites is summarized in Table 5. A lower M_n is obtained with phosphine ligands (M_n=375—550) than with phosphite ligands (M_n=1200); this fact indicates that the molecular weight regulation is stronger with more electron-donative phosphine than with less donative phosphite. In other words, hydrogenolysis of the Ni–polymer terminal bonding takes place more easily when the electronic density on the nickel atom is higher.

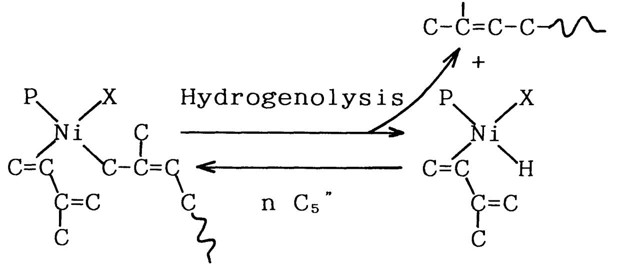


Fig. 5. Estimated mechanism of molecular weight regulation by H_2 via hydrogenolysis.

Hydrogenation of Liquid Polyisoprene. Since liquid polyisoprene with 1,4-microstructure has many methyl group branches, the hydrogenated liquid polyisoprene is supposed to have good rheological properties, like squalane, which is the hydrogenated product of natural triterpene, squalene. The results of hydrogenation are summarized in Table 6. A heterogeneous hydrogenation catalyst, such as Pd/Al_2O_3 or Raney Ni gives a quantitatively hydrogenated product at relatively high temperature (150—200 °C). On the other hand, a homogeneous nickel catalyst, such as $Ni(naph)_2/AlEt_3$/Hexamethylphosphoric triamide ($O=P(NMe_2)_3$) catalyst, exhibits high hydrogenation activity at a relatively low temperature (80 °C).

Attempt of One-Pot Synthesis of Hydrogenated Liquid Polyisoprene. Considering the above mentioned results that the $Ni(naph)_2/AlEt_3/O=P(NMe_2)_3$ catalyst (Catalyst A) works well as a homogeneous hydrogenation catalyst, a one-pot synthesis of hydrogenated liquid polyisoprene was examined. The results, however, were negative (Table 7), because catalyst A necessitates BTC to be an activator for the polymerizaiton of isoprene, whereas BTC inhibits the hydrogenation of liquid polyisoprene. These results indicate that a higher electronic density on the nickel

Table 5. Molecular Weight Control of Liquid Polyisoprene by H_2 (**2**) Influences of Phosphorous Ligands[a)]

No.	Ligand	Polymer yield/%	η	M_n	Microstructure/%[b)]			
			cp		*cis*-1,4-	*trans*-1,4-	1,2-	3,4-
1	$P(C_6H_5)_3$	85.3	28.5	375	53.5	30.8	0.9	14.8
2	$P(^nBu)_3$	78.4	75.4	550	52.4	32.7	1.1	13.8
3	$P(NMe_2)_3$	52.6	67.7	520	54.5	31.6	1.0	12.9
4	$P(OC_6H_5)_3$	98.2	1200	2300	62.8	27.6	0.4	9.2

a) Catalyst; $Ni(naph)_2(1)/AlEt_3(10)/BTC(5)$/ligand(1) ( ); molar ratio. $Ni(naph)_2$/isoprene=3.47×10^{-4} (molar ratio), Polymerization=60 °C, 12 h. b) At 30 °C. c) By Binder's method.[3)]

Table 6. Hydrogenation of Liquid Polyisoprene

No.	Hydrogenation catalyst		P_{H_2}	Temp	Time	Degree/%[a)] of hydrogenation
	Catalyst	Amount/wt%	atm	°C	h	
1	5%-Pd/Al_2O_3	5.0	30	150	2.5	≧99.9
2	Raney Ni	10.0	50	200	2.5	≧99.9
3	$Ni(naph)_2/AlEt_3$/HMPT[b)]		25	80	8.0	≧99.9

a) Calculated from Iodine value. b) Molar ratio=1/15/6, Ni/liquid polyisoprene=9.3×10^{-3} (molar ratio). HMPT=Hexamethylphosphoric triamide; $O=P(NMe_2)_3$.

Table 7. Trial of One-Pot Synthesis of Hydrogenated Liquid Polyisoprene

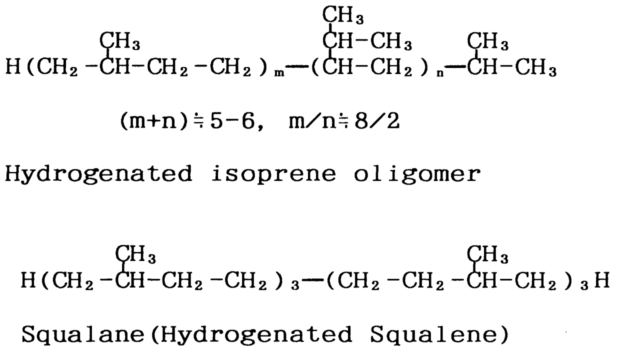
Catalyst	Polymerization	Hydrogenation
$Ni(naph)_2/AlEt_3$/BTC/HMPT[a)]	Yes	No
$Ni(naph)_2/AlEt_3$/HMPT[a)]	No	Yes

a) HMPT=Hexamethylphosphoric triamide; $O=P(NMe_2)_3$.

Table 8. Typical Properties of Hydrogenated Liquid Polyisoprene. Comparison with Squalane

Physical properties	Hydrogenated liquid polyisoprene	Squalane
Specific gravity/d_4^{20}	0.810	0.809
Refractive index/n^{20}	1.455	1.457
Iodine value/KOH mg g^{-1}	0.1	0.1
Molecular weight/M_n	425	420
Boiling point/°C	345	350
Flash point/°C	210	218
Viscosity/cp/20°C	21.8	21.6
Cloud point/°C	−20	−20
Solidifying point/°C	−65	−65
Surface tension[a)]/dyn cm^{-1}	34.0	34.3

a) 1 dyn=10^{-5} N.



$$H(CH_2-CH(CH_3)-CH_2-CH_2)_m-(CH(CH(CH_3)-CH_3)-CH_2)_n-CH(CH_3)-CH_3$$

(m+n)≒5-6, m/n≒8/2

Hydrogenated isoprene oligomer

$$H(CH_2-CH(CH_3)-CH_2-CH_2)_3-(CH_2-CH_2-CH(CH_3)-CH_2)_3H$$

Squalane (Hydrogenated Squalene)

Fig. 6. Structual formula of hydrogeneted isoprene oligomer and squalane.

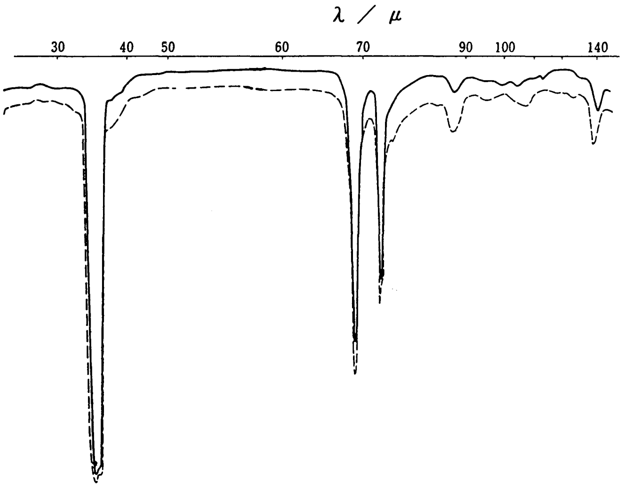


Fig. 7. IR spectra of Hydrogenated isoprene oligomer (——) and Squalane (------).

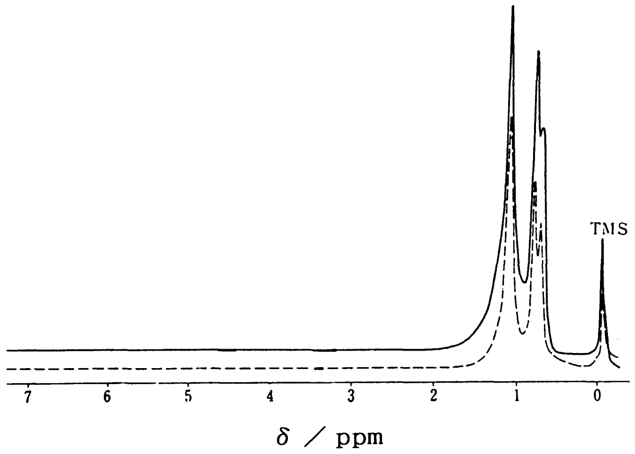


Fig. 8. NMR spectra of hydrogenated isoprene oligomer (——) and squalane (------).

atom is necessary for hydrogenation, whereas a lower electronic density is required for polymerization.

Comparison of Hydrogenated Liquid Polyisoprene with Natural Squalane. The microstructure of liquid polyisoprene consists of 85% the 1,4- and 15% the 3,4-structure (Table 3). Therefore, the molecular formula of the hydrogenated one has been estimated, as illustrated in Fig. 6, where the molecular formula of squalane is also shown. To adjust the molecular weight distribution, the low- and high-boiling components of hydrogenated liquid polyisoprene were cut off by high vaccum distillation; the thus-obtained saturated oil (SSC) exhibited very similar physical properties to those of the natural squalane, as shown in Table 8.[4)] The IR and NMR spectra of SSC also showed good similarity to those of squalane (Figs. 7 and 8).

Conclusions

In conclusion, we have revealed that a lower α-olefin (C_2', C_3') and hydrogen effectively lower the molecular weight of liquid polybutadiene and liquid polyisoprene by a nickel-containing Ziegler-type catalyst. The mechanism of molecular weight regulation involves β-hydride elimination for an α-olefin and hydrogenolysis for hydrogen. The hydrogenated low molecular weight oligomer of isoprene exhibits good similarity to squalane, which is a hydrogenated product of natural triterpene, squalene.

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