Homogeneous Polymerization of Butadiene Catalyzed by Ruthenium Complex–Tertiary Phosphine System

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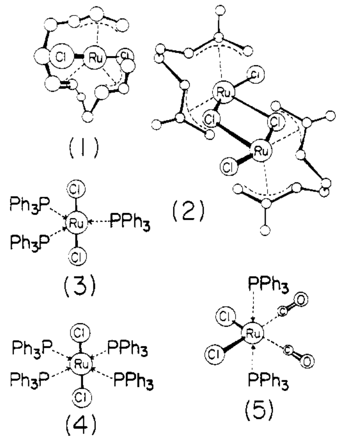
ABSTRACT: Butadiene has been polymerized in high conversion by use of dichloro(dodeca-2,6,10-triene-1,12-diyl)ruthenium(IV)- or dichlorodi-μ-chloro-bis(2,7-dimethylocta-2,6-diene-1,8-diyl)diruthenium(IV)–tertiary phosphine catalyst in a homogeneous solution. The microstructure of the resulting polybutadiene has *cis*-1,4-, *trans*-1,4-, and 1,2-unit contents of 37–60, 20–32, and 13–34%, respectively, whereas the molecular weight is $2.6\text{–}4.8 \times 10^3$. The nmr spectra of the catalysts, which are regarded themselves as active models of a growing end of the polybutadiene, are investigated in detail. With addition of triphenylphosphine to **1** or **2**, the π-allylic structure in **1** or **2** is converted into a σ-allylic one. A yellow-orange complex, dichloro(tri-*n*-butylpohsphine)-(dodeca-2,6,10-triene-1,12-diyl)ruthenium(IV) (**10**), which is yielded from **1** and tri-*n*-butylphosphine in toluene, contains a σ,π-allylic structure and is also active for the polymerization of butadiene in methylene chloride.

Canale and his coworkers[1] reported that ruthenium(III) chloride–tertiary phosphine catalysts polymerized butadiene in an aqueous emulsion. Ruthenium(III) chloride catalyst was also reported to polymerize cyclobutenes,[2] norbornenes,[3,4] and allene[5] in the aqueous emulsion or in alcohol. The propagation reaction in these polymerization systems proceeded in heterogeneous states, since the resultant polymers were deposited in the polar media. In addition, the reactions among the catalyst components and the monomer or the solvent were so complicated that the mechanisms of the polymerizations have not yet been elucidated clearly.

We have already reported the homogeneous polymerization of butadiene using a tertiary phosphine–dichloro(dodeca-2,6,10-triene-1,12-diyl)ruthenium(IV) (**1**) catalyst (Chart I).[6] As this catalyst contained three units of the monomer in itself, it was regarded as an active model of a growing end of polybutadiene. Accordingly, the nuclear magnetic resonance (nmr) spectra of the catalyst were investigated in detail, in order to elucidate the mechanism of a coordinated anionic polymerization of butadiene with this catalyst. In comparison with this catalyst, dichlorodi-μ-chloro-bis(2,7-dimethylocta-2,6-diene-1,8-diyl)diruthenium(IV)–triphenylphosphine catalyst and a few ruthenium(II)–triphenylphosphine complexes have been examined.

Chart I



Experimental Section

Materials. **1** was synthesized in the manner described by Shaw and his coworkers.[7] The procedure to prepare **2** was modified from the method of Porri, *et al.*,[8] as follows. In a 40-ml ampoule, 1 g of ruthenium(III) chloride trihydrate was dissolved in 13 ml of 2-methoxyethanol. After adding 14 ml of isoprene to this solution, the ampoule was sealed off and set in a water bath at 60° for 24 hr. A dark violet precipitate was collected, washed with ether, and dried *in vacuo*. Ruthenium(II)–triphenylphosphine complexes, **3**, **4**, and **5**, illustrated in Chart I, were prepared according to Wilkinson and Stephensons' methods.[9] Toluene and methylene chloride each were purified in the conventional manner.

Procedure of Polymerization. The catalyst components and methylene chloride were put into a 25-ml ampoule, which had previously been filled with dry nitrogen. In the case of toluene as solvent, however, **1** was dissolved in the solvent at first and then tertiary phosphine was added to the solution. The solution in the ampoule was degassed at a liquid nitrogen temperature by use of a conventional vacuum line. Butadiene was purified by passage over Molecular Sieve 5A, liquidized, and then redistilled into the ampoule. The ampoule was sealed off and set in a water bath controlled at a constant temperature. The reaction product was poured into an excess amount of methanol–hydrochloric acid mixture after a predetermined time. The sedimented polymer, pasty and dark yellow or amber, was washed with methanol and dried in a vacuum drier. The molecular weight of the polymer was measured with a Mechro Labo's

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[1] A. J. Canale, H. A. Hewett, T. M. Shryne, and E. A. Youngman, *Chem. Ind.* (London), 1054 (1962).

[2] G. Natta, G. Dall'Asta, and L. Porri, *Makromol. Chem.*, **81**, 253 (1964).

[3] F. W. Michelotti and W. P. Keaveney, *J. Polym. Sci., Part A*, **3**, 895 (1965).

[4] R. E. Rinehart and H. P. Smith, *ibid., Part B*, **3**, 1049 (1965).

[5] S. Otsuka, A. Nakamura, and K. Tani, *Kogyo Kagaku Zasshi*, **70**, 2007 (1967).

[6] K. Hiraki and H. Hirai, *J. Polym. Sci., Part B*, **7**, 449 (1969).

[7] J. E. Lydon, J. K. Nicholson, B. L. Shaw, and M. R. Truter, *Proc. Chem. Soc. London*, 421 (1964).

[8] L. Porri, M. C. Gallazzi, A. Colombo, and G. Allegra, *Tetrahedron Lett.*, 4187 (1965).

[9] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 945 (1966).

TABLE I
POLYMERIZATION OF BUTADIENE WITH 1-TRIPHENYLPHOSPHINE CATALYST[a]

PPh$_3$/Ru mol ratio	Solvent[b]	Temp, °C	Polymer obtained: Yield, %	Mol wt × 10^{-3}	Microstructure, %: cis	trans	1,2
0	T	30	0				
1	T	30	30	4.7	54	31	15
2	T	30	93	4.8	60	26	14
5	T	30	75	2.6	58	28	14
10	T	30	75				
2	T	50	99	2.8	54	28	18
5	T	50	90	2.6	50	31	19
1	MC	50	88				
2	MC	50	99	3.3	34	32	34
5	MC	50	90	2.8	41	29	30

[a] Conditions: **1**, 0.10 mmol; butadiene, 3.0 ml; solvent, 8.0 ml; reaction time, 24 hr. [b] T, toluene; MC, methylene chloride.

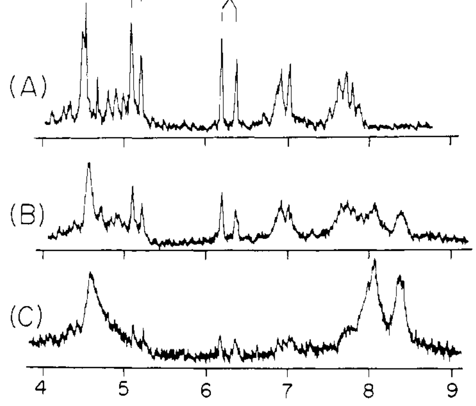
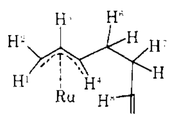
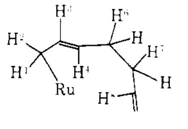


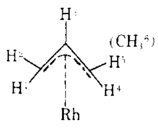
Figure 1. Nmr spectra of **1**-triphenylphosphine system: (A) **1**; (B) **1**:PPh$_3$ = 1:1; (C) **1**:PPh$_3$ = 1:2; conditions, 60 Mcps, 22°, in chloroform.

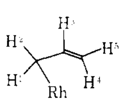
TABLE II
THE NMR DATA[a] OF THE ALLYLIC GROUPS IN RuCl$_2$(C$_{12}$H$_{18}$) (1) AND THE RELATED COMPOUNDS[b]

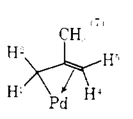
Line	Compd	Type[c]	τ_1	τ_2	τ_3	τ_4	τ_5	τ_6	τ_7	τ_8
1	RuCl$_2$(C$_{12}$H$_{18}$) (**1**)	A-π	6.24 d	5.11 d	4.4 m	4.8 m[d]		7.6 m[d]	6.9 m[d]	4.51
2	RhCl(1-methylallyl)(C$_5$H$_5$)[e]	A-π	7.39 d	5.57 d	5.09 m	6.22 m		8.17 m		
3	RuCl$_2$(C$_{12}$H$_{18}$) + 2PPh$_3$	σ	8.40 b	8.40 b	4.55	4.55		8.03 b	8.03 b	4.55
4	Rh(σ-allyl)(π-allyl)(C$_5$H$_5$)[e]	σ	8.22 m	8.22 m	3.83	5.3 m	5.3 m			
5		S-π	8.95 d	6.45 d	5.3	8.95 d	6.45 d			
6	RuCl$_2$(C$_{12}$H$_{18}$)·P(*n*-Bu)$_3$ (**10**)	σ,π	7.9 b	7.9 b	6.03	6.54 d		7.6 m[d]	6.9 m[d]	4.96
7	PdCl(2-methylallyl)(PPh$_3$)[f]	σ,π	7.5 d	7.5 d		6.5 d	5.5 d		(8.5)	











[a] Measured in deuteriochloroform at 60 Mcps. Coupling constants and C$_5$H$_5$, phenyl, and *n*-butyl resonances all are not given in this table; b = broad, d = doublet, m = multiplet. [b] Protons numbered are shown below this table. [c] A-π = asymmetric π-allyl; S-π = symmetric π-allyl. [d] The coupling of the protons was not analyzed. [e] The data of J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 583 (1968). [f] The data of J. Powell, S. D. Robinson, and B. L. Shaw, *Chem. Commun.*, 78 (1965).

Model 301A vapor pressure osmometer in toluene solution. The microstructure of the polymer was analyzed according to the method of Silas, *et al.*[10]

Measurement of Nmr Spectra. The nmr spectra of the complexes and of catalyst systems were measured using a Japan Electron Optics Laboratory's Model C-60 spectrometer, operating at 60 Mcps.

Reaction between 1 and Tri-*n*-butylphosphine. To 68 ml of the toluene solution containing 2.0 mmol of **1**, 18 ml of a toluene solution containing 2.1 mmol of tri-*n*-butylphosphine was added at room temperature under nitrogen atmosphere. The color of the solution changed from yellow-orange to dark red. After several minutes, a yellow-orange precipitate was yielded. The precipitate was collected, washed with *n*-hexane, and dried *in vacuo*. This precipitate was fairly sensitive to air.

Anal. Calcd for C$_{24}$H$_{45}$Cl$_2$PRu: C, 53.72; H, 8.45. Found: C, 52.97; H, 8.08.

Results

1. The System Derived from 1 and Triphenylphosphine. Table I shows the results of polymerization of butadiene catalyzed by the **1**-triphenylphosphine system. **1** itself did not polymerize butadiene at all, owing to the sluggishness of the π-allylic structure toward successive insertion of butadiene monomer. However, **1** was found to become an active catalyst for the polymerization of butadiene through a reaction with triphenylphosphine. The catalytic activity of the system for the polymerization was considerably high at molar ratios of triphenylphosphine-**1** of 2:5. The *cis*-1,4-unit content of the resulting polybutadiene obtained at 50° was lower by about 10% than that of the polymer yielded at 30° in toluene solution.

The reaction between **1** and triphenylphosphine was well demonstrated by color change of the solution (yellow to orange) and by nmr spectra shown in Figure 1. The nmr spectrum of **1**, exhibiting two sharp doublets at τ 5.1 and 6.24 and a multiplet near 4.6, distinctly indicated the existence of π-allylic group,[7] and was analyzed, as shown in the first line in Table II, by comparison with nmr data of chloro(1-methyl-π-allyl)cyclopentadienylrhodium(III)[11] in the second line.

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(10) R. Silas, J. Yates, and V. Thorton, *Anal. Chem.*, 529 (1959).

(11) See Table II, footnote *e*.

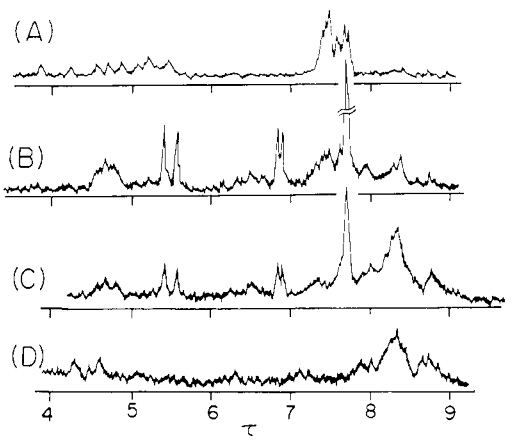


Figure 2. Nmr spectra of **2**–triphenylphosphine system: (A) **2**; (B) **2**:PPh_3 = 1:2. The intensity of the methyl protons at τ 7.75 is three times as large as that of the doublet at 5.51 or 6.90; (C) **2**:PPh_3 = 1:4; (D) **2**:PPh_3 = 1:6; conditions, 60 Mcps, 20°, in deuteriochloroform.

TABLE III
POLYMERIZATION OF BUTADIENE WITH
2–TRIPHENYLPHOSPHINE CATALYST[a]

PPh_3/**2** molar ratio	Polymer obtained Yield, %	Mol wt × 10^{-3}	Microstructure, % *cis*	*trans*	1,2
0	0				
2	9				
4	99		36	32	32
6	97	2.9	37	30	33
10	99	3.0			

[a] Conditions: **2**, 0.05 mol; butadiene, 3.0 ml; methylene chloride, 8.0 ml; reaction, at 50°, 24 hr.

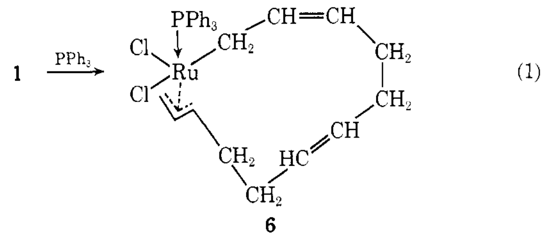
TABLE IV
POLYMERIZATION OF BUTADIENE IN THE
PRESENCE OF **3**, **4**, AND **5**[a]

Complex	Temp, °C	Polymer obtained Yield, %	Mol wt × 10^{-3}	Microstructure, % *cis*	*trans*	1,2
3	60	99	2.8	42	26	32
4	30	80	4.2	50	24	26
5	60	0				

[a] Conditions: the ruthenium complex, 0.10 mmol; butadiene, 3.0 ml; solvent, methylene chloride of 8.0 ml; reaction time, 24 hr.

Figure 1B illustrates the nmr spectrum of the system derived from equal moles of **1** and triphenylphosphine, indicating the coexistence of both π-allylic structure and a new type of allylic one corresponding to new signals at τ 4.55, 8.03, and 8.40, seen in Figure 1C.

Figure 1C shows the nmr spectrum of the system derived from 1 mol of **1** and 2 mol of triphenylphosphine. The signals at τ 4.55 and 8.03 are attributed to olefinic protons in $-CH{=}CH-$ and allylic methylene protons ($-CCH_2C{=}C-$), respectively. The other signal at 8.40 can be ascribed to protons of allylic structures adjacent to the ruthenium atom ($RuCH_2C{=}C-$). This τ value was very close to that of methylene protons of σ-allylic group in (σ-allyl)(π-allyl)cyclopentadienylrhodium(III),[11] as shown in the fourth line in Table II. In addition, the spectrum seen in Figure 1C was quite different from that of authentic *trans,trans,trans*-cyclododeca-1,5,9-triene, and lacked vinyl protons ascribed to 8-vinylcyclodeca-1,5-diene. Consequently, the dodeca-2,6,10-triene-1,12-diyl ($C_{12}H_{18}-$) group was combined to the ruthenium atom through two σ-allylic bonds, in the system derived from **1** and 2 mol of triphenylphosphine. Accordingly, the reactions between **1** and triphenylphosphine are formulated as



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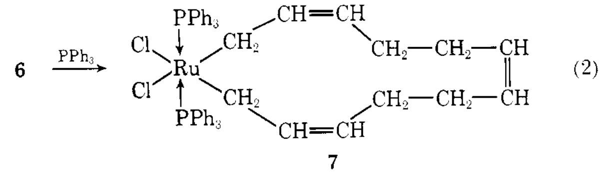

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where the relative position of each ligand in **6** and **7** is arbitrary. Such conversion of π-allylic structure into σ-allylic one with addition of tertiary phosphine was reported for bis(2-methyl-π-allyl)nickel[12] and di-μ-chloro-di(1-methyl-π-allyl)dipalladium(II).[13]

2. The System Derived from 2 and Triphenylphosphine. Table III shows the results of polymerization of butadiene catalyzed by **2**–triphenylphosphine system. **2** itself was quite inactive for the polymerization of butadiene like **1**, as **2** also had stable π-allylic structure.[8] Figure 2 demonstrates nmr spectra of the system derived from **2** and triphenylphosphine. As seen in Figure 2A, **2** itself has a complicated nmr spectrum, which has not yet been analyzed.

Figure 2B illustrates a nmr spectrum of the system derived from **2** and 2 mol of triphenylphosphine. The splittings in two doublets at 5.51 and 6.90 are caused by couplings with a phosphorus atom coordinated to the ruthenium atom. This kind of pattern in the nmr spectrum represents the formation of a new kind of complex containing 2-methyl-π-allylic structure, similarly to $RuCl_2(C_{10}H_{16})(CO)$[8] or $RuCl_2(C_{10}H_{16})$(pyridine).[8] This system had only a low activity for polymerization of butadiene.

Figures 2C and -D exhibit nmr spectra of the systems derived from **2** and 4 and 6 mol of triphenylphosphine, respectively. Figure 2C indicates the formation of a new type of 2-methylallylic structure corresponding to new signals at 8.11, 8.55, and 8.96, shown also in Figure 2D, besides the 2-methyl-π-allylic structure. In Figure 2D, four signals at 4.65 (ambiguous in Figure 2C), 8.11, 8.55, and 8.96 indicate that the 2,7-dimethylocta-2,6-diene-1,8-diyl ($C_{10}H_{16}$) group in this system is joined

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[12] G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter, and H. Zimmermann, *Angew. Chem.*, **78**, 157 (1966).

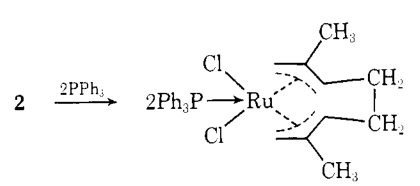
[13] M. L. H. Green, "Organometallic Compounds," 3rd ed, Vol. II, Methuen and Co., London, 1968, p 54.

TABLE V
POLYMERIZATION OF BUTADIENE WITH 1–TRI-*n*-BUTYLPHOSPHINE CATALYST[a]

				Polymer obtained				
						Microstructure, %		
Complex	P/Ru mol ratio	Solvent[b]	Temp, °C	Yield, %	Mol wt × 10^{-3}	*cis*	*trans*	1,2
1	1	T	50	0[c]				
1	3	T	30	0[c]				
1	5	T	50	0[c]				
1	1	MC	50	18	1.6			
1	2	MC	52	82	3.7	54	20	26
1	5	MC	52	8.7				
10	1[d]	MC	60	83	2.8	49	24	27

[a] Conditions: **1** or **10**, 0.10 mmol; butadiene, 3.0 ml; solvent, 8.0 ml; reaction time, 24 hr. [b] T, toluene; MC, methylene chloride. [c] The yellow-orange precipitate was yielded. [d] Evaluated on the tri-*n*-butylphosphine coordinated in **10**.

to the ruthenium atom through two 2-methyl-σ-allylic bonds, analogously to the $C_{12}H_{18}$ group in the **1**–triphenylphosphine system. The reactions between **2** and triphenylphosphine are summarized as



(3)

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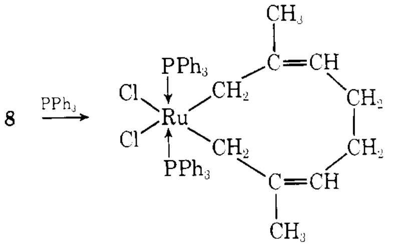

(4)

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where the relative position of each ligand in **8** and **9** is arbitrary. **2** had a high activity for polymerization of butadiene in the presence of more than 4 mol of triphenylphosphine (see Table III), similarly to **1**.

3. Ruthenium(II)–Triphenylphosphine Complexes. Table IV shows the results of polymerization runs, in the presence of **3**, **4**, or **5**. The former two complexes had a fairly high activity for polymerization of butadiene, and yielded polybutadiene having a similar microstructure and a similar molecular weight to those obtained with the **1**–triphenylphosphine system, respectively. **5**, which had no available site for coordination of other ligand, was actually inactive for polymerization of butadiene.

4. The System Derived from 1 and Trialkylphosphine. The **1**–tri-*n*-butylphosphine system in toluene yielded a yellow-orange precipitate and produced no polymer. This catalyst system in methylene chloride, however, was homogeneous and active for polymerization of butadiene, as shown in Table V. The microstructure and the molecular weight of the resulting polymer were similar to those observed with the **1**–triphenylphosphine system, respectively. The addition of excess amount of tri-*n*-butylphosphine to **1** decreased the polymerization activity, in contrast to the case of the **1**–triphenylphosphine system.

The yellow-orange precipitate, isolated from the reaction between equimolar quantities of **1** and tri-*n*-butylphosphine in toluene, exhibited a nmr spectrum, containing both three signals at τ 9.15, 9.08, and 8.59 attributable to *n*-butyl group and complicated signals ascribed to the $C_{12}H_{18}$ group (*vide infra*), as illustrated in Figure 3. On the grounds of this evidence and of the elemental analysis, this precipitate was assigned to a complex, $[RuCl_2(C_{12}H_{18})\cdot P(n\text{-}C_4H_9)_3]$ (**10**). The infrared spectrum (KBr disk) of **10** had a weak band at 1660 cm^{-1} and a medium band at 1622 cm^{-1}, both attributable to carbon–carbon double bonds, while **1** itself exhibited a medium band at 1522 cm^{-1}, assigned to a carbon–carbon double bond coordinated to the ruthenium.[7]

The nmr spectrum of the $C_{12}H_{18}$ group in **10** showed four kinds of new signals, *i.e.*, a singlet at τ 6.03, a doublet at 6.54, and two broad signals at 4.96 and 7.8–8.05, in place of the characteristic signals of the π-allylic structures (Figure 1A). The three signals at 6.03, 6.54, and 4.96 with the intensity of one were attributed to protons 3, 4, and 8 in the $C_{12}H_{18}$ group, respectively, as seen in the sixth line in Table II, whereas the broad signal at 7.8–8.05 with the intensity of two was ascribed to proton 1 and 2. Furthermore, the τ value of the proton 4 and the splitting of the signal in **10** were very similar to the corresponding ones, respectively, of chloro(2-methyl-σ,π-allyl)(triphenylphosphine)palladium(II), in which both σ- and π-coordinations of the 2-methyl-

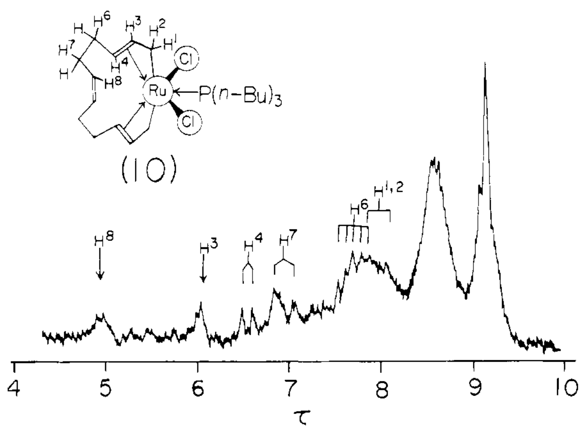


Figure 3. Nmr spectrum of $[RuCl_2(C_{12}H_{18})\cdot P(n\text{-}Bu)_3]$, **10**; conditions, 60 Mcps, 25°, in deuteriochloroform.

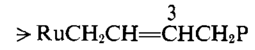
allyl group to the palladium[14] were confirmed by X-ray analysis.[15] Of course, the $C_{12}H_{18}$ group in **10** was not cyclized to the cyclododeca-1,5,9-triene or 8-vinylcyclodeca-1,5-diene, by the same reasons as those described in the **1**–triphenylphosphine system. On the basis of these evidences, the $C_{12}H_{18}$ group in **10** was coordinated with the ruthenium atom through two σ,π-allylic bonds rather than through two σ-allylic ones. **10** also polymerized butadiene with a fairly high yield in methylene chloride.

5. The System Derived from 1 and Other Lewis Bases. The system derived from **1** and triphenylarsine was poorly active and yielded only a trace of polymer, although this Lewis base was similar in structure to triphenylphosphine. Triphenyl phosphite, tri-*n*-butyl phosphite, dodecyl phosphonotrithioite, and diphenyl sulfide each was ineffective as a cocatalyst for **1** to polymerize butadiene. The nmr spectrum of the system derived from **1** and 2 mol of triphenylarsine or 2 mol of triphenyl phosphite showed no recognizable change from the spectrum of the π-allylic structures in compound **1**.

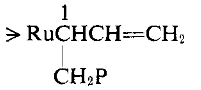
Discussion

Dichlorobis(substituted π-allyl)ruthenium(IV), **1** and **2**, each itself was quite inert for the polymerization of butadiene, in contrast with π-allylic complexes of the first series transition metals, *i.e.*, titanium,[16] chromium,[12] cobalt,[12] and nickel.[12,17] However, the **1**– or **2**–tertiary phosphine system was an active catalyst for the polymerization of butadiene in the homogeneous solution. The microstructure of the resultant polymer was distinctly different from that of polybutadiene obtained with a radical,[18] an anionic,[19] or a cationic catalyst.[20] In addition, both the **1**– and **2**–tertiary phosphine systems polymerized norbornene with a very high conversion.[21] These facts indicate that these catalyst systems polymerize butadiene through a coordinated anionic mechanism.

The reaction product between **1** and 2 mol of triphenylphosphine was not only an active intermediate for the polymerization of butadiene, but also an active model of a growing end of polybutadiene containing three units of the monomer, while **1** itself was regarded as a stable model of an intermediate in a catalytic cyclotrimerization of butadiene.[7] The nmr spectra of the **1**–triphenylphosphine system showed that the initial π-allylic structures in **1** were converted into the σ-allylic ones with the addition of triphenylphosphine (see Figure 1). With the coordination of triphenylphosphine, these σ-allylic bonds are more activated than the initial π-allylic ones, while the σ-allylic bonds are stable for polymerization of 50–90 units of butadiene.[22] On the ground of these discussions, the propagation reaction in this polymerization was considered to proceed through a successive insertion of butadiene monomers into the active ruthenium–allylic bonds. The polymer obtained with this catalyst system included 13–34% of the 1,2-unit, which could not result from a 3-substituted σ-allyl structure, as shown in **11**. Accordingly, the growing end of the polybutadiene with this catalyst virtually might contain the corresponding amount of a 1-substituted σ-allyl structure, **12**, to that of the 1,2-unit content in the resulting polymer, or might have some extent of a dynamic allyl character.[23,24]


$>\mathrm{RuCH_2CH}{=}\overset{3}{\mathrm{C}}\mathrm{HCH_2P}$

11


$>\mathrm{Ru}\underset{\mathrm{CH_2P}}{\overset{1}{\mathrm{C}}}\mathrm{HCH{=}CH_2}$

12

The **2**–triphenylphosphine system also had almost the same activity for polymerization of butadiene as the **1**–triphenylphosphine system had. The former system, however, required more moles of triphenylphosphine by 1 mol per the ruthenium atom than the latter system did, since **2** combined 2 mol of triphenylphosphine to be converted into 2 mol of the monomeric species, **8**. The nmr spectra of the **2**–triphenylphosphine system indicated that with the addition of 6 mol of triphenylphosphine the 2-methyl-π-allylic structures in **2** were also converted into the active 2-methyl-σ-allylic structures capable of polymerizing butadiene, analogous to the π-allylic structures in **1**.

10 was isolated from the toluene solution of **1** and tri-*n*-butylphosphine, and was also an active intermediate for the polymerization of butadiene. The $C_{12}H_{18}$ group in **10** was coordinated with the ruthenium atom through the two σ,π-allylic bonds rather than through the two σ-allylic bonds, as indicated above on the basis of the nmr data. Accordingly, these σ,π-allyl–ruthenium bonds were able to initiate the polymerization of butadiene. However, it is ambiguous whether a growing end of polybutadiene catalyzed by **10** held the σ,π-allylic structures or changed to the σ-allylic ones. In **10**, the tri-*n*-butylphosphine ligand may be coordinated to the ruthenium at the site which the carbon–carbon double bond had occupied in **1**, since the coordination of the phosphine had accompanied the decrease of the infrared band at 1522 cm^{-1}.

The molecular weight of the polymers obtained with the **1**– and **2**–triphenylphosphine systems were 2.6–4.8 × 10^3, indicating that the polymer chain consisted of 50–90 units of butadiene, while the initial molar ratio of butadiene to the ruthenium atom was 400. This means that a chain transfer occurred several times per the ruthenium atom, if all the complex was effective for the polymerization in the homogeneous solution. An infrared spectrum of the pasty polybutadiene exhibited very weak coupled bands at 1943 and 1978

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(14) See Table II, footnote *f*.

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cm^{-1}, attributable to allene structure. This suggests a hydrogen transfer from one allylic group to the other in the termination in this polymerization, as proposed in the termination in the polymerization of cyclobutenes catalyzed with ruthenium(III) chloride.[2]

3 and **4** each converted butadiene to the polymer having similar microstructure and similar molecular weight to those obtained with the **1**–triphenylphosphine catalyst, respectively (see Table IV), while neither **3** nor **4** itself had a ruthenium–carbon bond. The facts stated above indicate that the propagation in the polymerization catalyzed by **3** or **4** proceeded through the almost same mechanism as that for the **1**–triphenylphosphine system. Accordingly, a ruthenium–carbon bond might be formed in the reaction of **3** or **4** with butadiene. This kind of the ruthenium–carbon bond formation may occur also in a reactivation process of the deactivated ruthenium species, which had presumably been produced in the termination reaction.

The tertiary phosphine, such as triphenylphosphine or tri-*n*-butylphosphine, was specific as the cocatalyst for **1** or **2** to polymerize butadiene, because triphenylarsine was never the effective cocatalyst in spite of the similarity of the structure between these two kinds of Lewis bases. Triaryl or trialkyl phosphite, alkyl phosphonotrithioite, or diaryl sulfide was also ineffective as the cocatalyst. In addition, triphenylarsine and triphenyl phosphite have a weaker σ-donating ability and a stronger π-accepting one than those of the tertiary phosphine, respectively.[25–27] These evidences indicate that the suitable degree of σ-donating ability and of π-accepting one, like those of tertiary phosphine, might be necessary for the activation of the π-allylic groups of **1** or **2** to polymerize butadiene.

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Polyquinoxalines Containing *p*-Phenylene Ether and *p*-Phenylene Moieties

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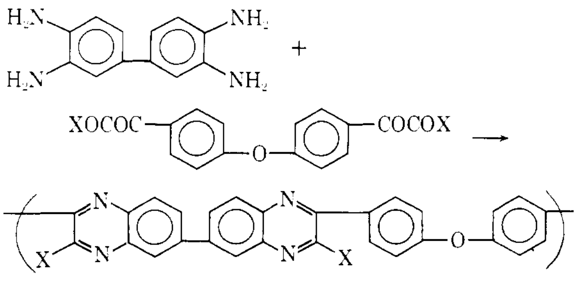
ABSTRACT: A series of quinoxaline polymers containing *p*-phenylene ether and *p*-phenylene moieties were prepared by polymerization of 3,3′-diaminobenzidine with various aromatic bisglyoxals in *m*-cresol. The glass transition temperature (T_g) of the polyquinoxalines varied from 133° for a polymer highest in *p*-phenylene ether content to 350° for a polymer containing rigid *p*-phenylene moieties. Ultraviolet and visible spectroscopic study showed the λ_{max} for the *p*-phenylene ether polymers to be about the same while pronounced bathochromic shifts in the λ_{max} were observed as the conjugated system was increased from *p*-phenylene to *p,p*′-biphenylene to *p,p*′-terphenylene in the *p*-phenylene polymers. Although thermal gravimetric analysis failed to show any distinct difference between the *p*-phenylene ether and the *p*-phenylene polymers, isothermal weight loss study at 400° in air showed that the *p*-phenylene polymers lost less weight after a given time than the *p*-phenylene ether polymers. Prior to polymer work, a series of quinoxaline model compounds was prepared to aid in polymer characterization.

Polyquinoxalines (PQ)[1–6] and polyphenylquinoxalines (PPQ)[7–9] have received considerable attention in recent years. These polymers are generally prepared by the reaction of an aromatic bis(*o*-diamine) such as 3,3′-diaminobenzidine with a bis(α-dicarbonyl) compound such as *p,p*′-oxybis(phenyleneglyoxal) or *p,p*′-oxydibenzil to yield a PQ or PPQ, respectively, as shown in eq 1.



X = H or C_6H_5 (1)

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