

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Initiation Reaction of the Alkali-Metal Catalyzed Polymerization of Dienes Bearing Allylic Protons

Hajime Yasuda<sup>a</sup>; Hisaya Tani<sup>a</sup>

<sup>a</sup> Department of Polymer Science Faculty of Science, Osaka University Toyonaka, Osaka, Japan

**To cite this Article** Yasuda, Hajime and Tani, Hisaya(1975) 'Initiation Reaction of the Alkali-Metal Catalyzed Polymerization of Dienes Bearing Allylic Protons', *Journal of Macromolecular Science, Part A*, 9: 6, 1007 – 1027

**To link to this Article:** DOI: 10.1080/00222337508081505

**URL:** <http://dx.doi.org/10.1080/00222337508081505>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Initiation Reaction of the Alkali-Metal Catalyzed Polymerization of Dienes Bearing Allylic Protons

HAJIME YASUDA and HISAYA TANI

Department of Polymer Science  
Faculty of Science  
Osaka University  
Toyonaka, Osaka 560, Japan

### ABSTRACT

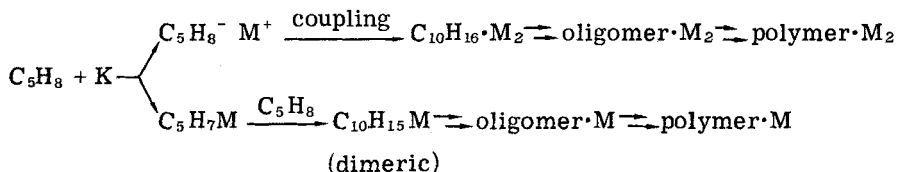
Initiation of the polymerization of dienes bearing allylic protons with metallic alkali metals were investigated. Addition of a tertiary amine into the solution resulted in the complete inhibition of the polymerization to give a mono- or dianionic dienylmetal compound and reduced dimers in quantitative yield. The planar conformations of the isolated dienyl alkali metal compounds, which are considered to be real active species toward the alkali-metal catalyzed polymerizations, were determined by PMR and  $^{13}\text{C}$  NMR spectroscopy. The catalytic activity toward polymerization as well as the chemical reactivity of those dienyl alkali metals was investigated.

## INTRODUCTION

Anionic polymerizations of dienes, especially those of butadiene, styrene, and isoprene with alkylolithium or arylalkali metals, have been extensively studied by many workers. Rate constants of the propagating chain ends, and association behavior of polystyryl-, polyisoprenyl-, or polybutadienyllithium were investigated in detail directly by PMR spectroscopy or by kinetics by Morton [1], Bywater [2], Hsieh [3], Urwin [4], and Makowski [5]. The effect of the alkyl-lithium structure, solvent type, temperature, and initiation level on polymer chemistry were further studied by others [6-10]. The polymerizations of styrene and butadiene in polar media with sodium naphthalene to induce living polymerization were precisely investigated by Szwarc and co-workers [11]. Their technique made it possible to measure the rate of propagation via an ion-pair independent of that via a free ion. In contrast to those spectacular works, the polymerizations of dienes with metallic alkali metals [12, 13], especially initiation of the polymerization of dienes bearing allylic protons, have received very little attention [14]. In the polymerization of dienes catalyzed by alkali metals, dianions derived from diene dimers have been considered to be a real active species. The reaction of butadiene with sodium metal in ammonia to give a butadiene dimer dianion was reported by Ziegler [14]. The corresponding reaction of isoprene with sodium naphthalene to give isoprene dimer dianions was reported by Suga [15]. Dimer dianion [16], as well as tetramer dianion [17] of  $\alpha$ -methylstyrene obtained from the monomer and an excess amount of potassium, is also known as a typical carbanion. This paper describes the isolation of a catalytically active species, the preparation and reaction of dienes bearing allylic protons (mainly 1,3-pentadiene) with metallic alkali metals (mainly potassium), and the structure of the dienyl anion of pentadienyl alkali metals. These works were done mainly from the viewpoint of synthetic chemistry.

## ISOLATION OF DIENYLALKALIMETAL COMPOUNDS

Polymerization of 1,3-pentadiene with a catalytic amount of an metallic alkali metal can be considered to proceed through a step-wise reaction:






where M is an alkali metal.

The first one is proceeded by a dianion type initiator formed by coupling of radical monoanions and other is proceeded by a monoanionic initiator. If this scheme is correct, the initiation product is expected to be caught by increasing the amount of alkali metal and/or by decreasing the reaction temperature. This expectation was realized.

The reaction of 1,3-pentadiene (0.1 mole) with metallic potassium (0.05 mole) dispersed in tetrahydrofuran (20 ml) was carried out at 0°C for 5 hr. By the addition of an excess amount of n-hexane into the reaction mixture, yellowish powdery pentadienylpotassium was obtained as a precipitate. Recrystallization from a mixture of THF and n-hexane gave needle crystals. Unreacted monomer, reduced dimer, and polymer were obtained from the n-hexane soluble fraction using an appropriate method. By increasing the reaction temperature and/or by decreasing the amount of metallic potassium, the yield of polymer increased rapidly. Other dienes also behaved similarly and gave corresponding dienylypotassium compounds (Table 1). 2,3-Dimethyl-1,3-butadiene and isoprene gave only polymers by the reaction with metallic potassium.

The addition of a tertiary amine into the reaction system resulted in the complete inhibition of the polymerization. The use of 1 mole equivalence of triethylamine, triethylenediamine, tetramethylethylenediamine, or tetramethylpropylenediamine was most effective for the inhibition of polymerization and gave quantitatively a mixture of dienylypotassium and the reduced dimer [18]. Pyridine or dipyridyl was less effective for this purpose. Thus the nature of a tertiary amine becomes a crucial factor for the successful preparation of dienyly alkali metal compounds. In contrast to our method, the reaction of conjugated dienes, 1,3-pentadiene, 2,4-hexadiene, 2-methyl-, and 4-methyl-1,3-pentadiene with n-butyllithium gave only polymers in place of the formation of the 1:1 dienyly metal compounds, even in the presence of a tertiary amine. Preparation of corresponding dienylylithium compounds were available only

TABLE 1. Conversion of Dienes by the Reaction with Metallic Potassium in a 1:1 Mole Ratio in THF for 5 hr<sup>a</sup>

Monomer	Reaction temperature (°C)	K-compound <sup>b</sup> (%)	Dimers <sup>c</sup> (%)	Oligomers <sup>d</sup> (%)	Recovered monomer (%)
C=C=C-C=C	-20	20	20	30	30
	0	16	17	58	9
	40	2	2	91	5
C=C-C-C=C	0	45	45	3	7
C=C=C-C=C-C	0	6	7	69	18
$\begin{array}{c} \text{C} \quad \text{C} \\   \quad   \\ \text{C}=\text{C}-\text{C}=\text{C} \end{array}$	0	0	0	96	4
	0	45	45	1	9
	0	43	46	1	10
	40	42	49	0	9

<sup>a</sup> Represented by mole % conversion of monomer.

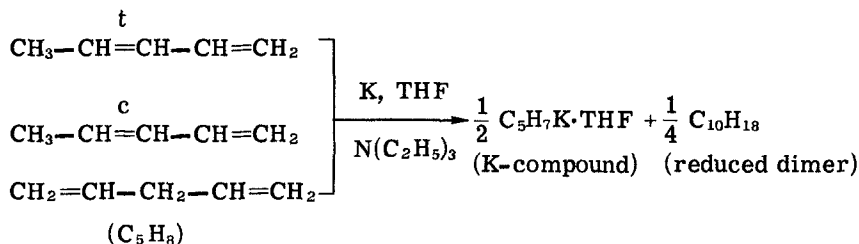
<sup>b</sup> Determined titrimetrically. The compound was isolated by cooling the reaction mixture after addition of an excess of n-pentane.

<sup>c</sup> Detected with glpc.

<sup>d</sup> Calculated by gravimetry.

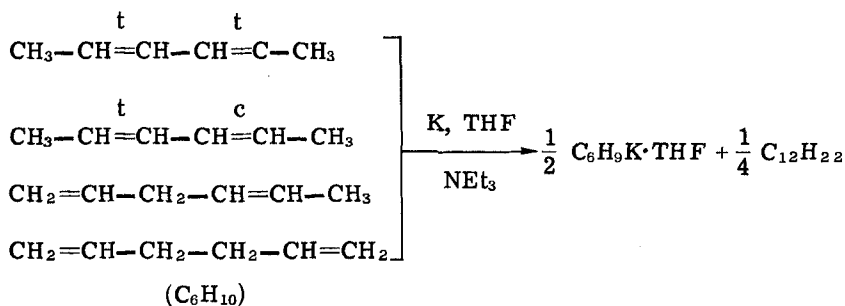
when unconjugated dienes [19], not conjugated ones [20], were reacted with *n*-butyllithium.

Reaction of *cis*-1,3-pentadiene, *trans*-1,3-pentadiene, or 1,4-pentadiene (1.5 mole) with metallic potassium (1.0 mole) in a mixture of tetrahydrofuran (2.0 mole) and triethylamine (1.0 mole) gave quantitative yields of crystalline pentadienylpotassium tetrahydrofuranate and a mixture of reduced pentadiene dimers following the stoichiometry represented by

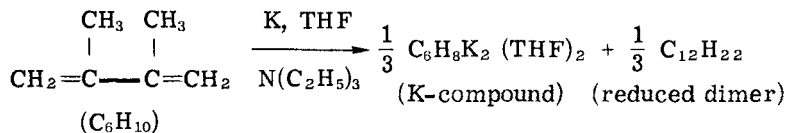


PMR and CMR spectra showed that the presence or the absence of a tertiary amine in the reaction system had no effect on the structure of the pentadienylpotassium compound.

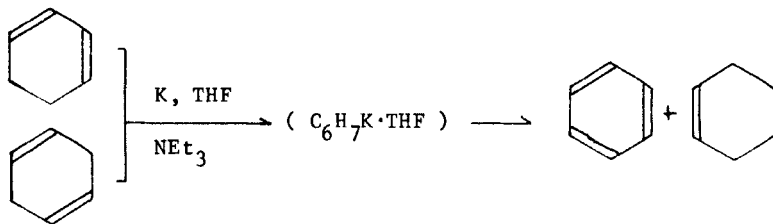
Similarly to the reactions of pentadienes, other dienes such as 2-methyl-1,3-pentadiene, 4-methyl-1,3-pentadiene, four isomers of *n*-hexadienes, two isomers of cycloheptadienes, and three isomers of cyclooctadienes gave the dienyl potassium tetrahydrofuranate and reduced dimers in 90 to 95% yields. In these cases an unconjugated diene required higher temperature than a conjugated one. For example, in the case of *n*-hexadienes, 1,5-hexadiene required a high temperature (50°C for 24 hr) for completion of the reaction, whereas the reaction of 1,4- or 2,4-hexadiene was completed at 30 or 0°C, respectively, in 5 hr:



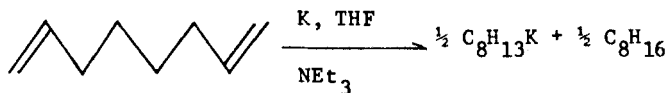
In contrast to these reactions, a monomer dianion was obtained from the reaction with 2,3-dimethyl-1,3-butadiene. The absence of a tertiary amine in the reaction system gave no 2,3-dimethyl-1,3-butadienylpotassium at all, but the addition of triethylamine produced 2,3-dimethyl-1,3-butadienyldipotassium and a reduced dimer, 2,3,6,7-tetramethyl-2,6-octadiene, in 47 and 50% yields, respectively.



In the cases of 1,3- and 1,4-cyclohexadiene, the dienyl compounds were not obtained by the reaction with potassium or sodium, and those dienes isomerized quantitatively to an equal amount of benzene and cyclohexene by allowing the mixture to stand at room temperature for 24 hr:



The migration of the double bond occurred only when the reactant has at least two olefinic groups. The reaction of 1-pentene, 2-pentene, 1-octene, or 2-octene with metallic potassium in tetrahydrofuran at 60°C for 4 days did not result in any migration, and the starting materials were recovered. In contrast to this, the double bonds of 1,7-octadiene, as with 1,5-hexadiene, were migrated to form 3,5-octadienyl- and 2,4-hexadienylpotassium, respectively. The active species for the migration of the double bond by metallic alkali



metal in tetrahydrofuran-tertiary amine was considered to be the same one as that of the dimethylsodium-dimethylsulfoxide [21] and potassium tert-butoxide-dimethylsulfoxide [22] system. The structures of reduced dimers obtained simultaneously with dienyl alkali metal compounds were determined by IR, mass and NMR spectroscopies. These were composed of the same isomeric mixture of hydrocarbons, irrespective of the positions of the double bonds in the starting hydrocarbons as shown in Table 2. These facts show that the double bond in the unconjugated diene would migrate to a conjugated position prior to reacting it with metallic potassium.

The anionic nature of the dienylpotassium compounds was obtained from the structures of the deuterolyses products (Table 3). All the dienylpotassium compounds were found to be monoanions, except for 2,3-dimethyl-1,3-butadienylpotassium in which the formation of a monomeric dianion was confirmed by deuterolysis. The stoichiometry was represented as referred to above in the equation. It is interesting to note that the potassium compounds of aliphatic 1,3-dienes, which are active monomers for anionic polymerization, gave 1,3-conjugated diene by hydrolyses, while cyclic 1,3-dienes, which are inactive toward anionic polymerization, gave 1,4-unconjugated cyclic dienes. The experimental results referred to above are qualitatively in accordance with our expectation of the polymerization of pentadiene with metallic potassium.

1,3-Pentadiene or 2,3-dimethyl-1,3-butadiene was selected as a typical example of the polymerization of a conjugated diene bearing allylic protons. The crystalline pentadienylpotassium behaved as a catalyst in the polymerization of 1,3-pentadiene to give results quite similar to those obtained with metallic potassium as shown in Table 4. This fact seems to suggest that the polymerization of 1,3-pentadiene catalyzed by metallic potassium in the absence of a tertiary amine proceeds through a monoanion as an initiating species. 2,3-Dimethyl-1,3-butadiene also behaved quite similarly. Thus pentadienylpotassium or 2,3-dimethyl-1,3-butadienylpotassium may be regarded as an active catalyst species.

#### CHEMICAL REACTIVITY OF DIENYL ALKALI METALS

Alkylations of the dienyl alkali metal compounds by methyl iodide and by tertiary-butylbromide were useful for understanding the



TABLE 2. Structure of Reduced Dimers


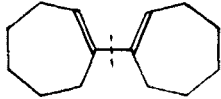

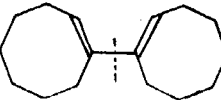
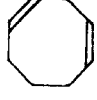
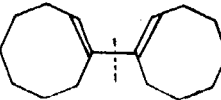
Diene	Reduced dimer	Mole ratio
$\overset{c}{C}-C=C-C=C$	$C-C-C-C=C-\overset{C}{\overset{t}{ }}-C-C=C-C$	7
$C-C=C-C=C$	$C-C-C=C-C-\overset{C}{\overset{t}{ }}-C-C=C-C$	7
$C=C-C-C=C$	$C-C=C-C-\overset{C}{\overset{t}{ }}-\overset{C}{\overset{t}{ }}-C-C=C-C$	5
$C-C=C-C=C-C$	$C-C-C=C-C-\overset{C}{\overset{t}{ }}-\overset{C}{\overset{t}{ }}-C-C=C-C$	11
$C-C=C-C-C=C$	$C-C=C-C-\overset{C-C}{\overset{t}{ }}-\overset{C}{\overset{t}{ }}-C-C=C-C$	8
$C=C-C-C-C=C$	$C-C-C=C-C-\overset{C}{\overset{t}{ }}-\overset{C}{\overset{t}{ }}-C-C=C-C$	7
$C-\overset{C}{\overset{t}{ }}-C=C-C=C$	$C-C-C=C-C-\overset{C}{\overset{t}{ }}-\overset{C}{\overset{t}{ }}-C-C=C-C$	2
	$C-\overset{C}{\overset{t}{ }}-C=C-C-\overset{C}{\overset{t}{ }}-\overset{C}{\overset{t}{ }}-C-C=C-C$	4
$C-\overset{C}{\overset{t}{ }}-C-\overset{C}{\overset{t}{ }}=C$	$C-\overset{C}{\overset{t}{ }}-C-C-\overset{C}{\overset{t}{ }}-\overset{C}{\overset{t}{ }}-C-C=C-C$	
		
		
		

TABLE 3. Deuterolysis of Dienylpotassium Compounds


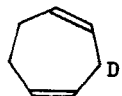



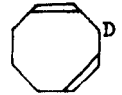
Diene	Deuterolysis
$\begin{array}{l} \text{C} \quad \quad (\text{cis}) \\   \\ \text{C}=\text{C}-\text{C}=\text{C} \quad (\text{trans}) \end{array}$	$\left. \begin{array}{l} \text{CD} \\   \\ \text{C}=\text{C}-\text{C}=\text{C} \\ \text{cis:trans} = 38:62 \end{array} \right\}$
$\begin{array}{l} \text{C} \\    \\ \text{C}-\text{C}-\text{C}=\text{C} \end{array}$	
$\begin{array}{l} \text{C} \quad \quad \text{C} \quad (\text{trans-trans}) \\   \quad \quad   \\ \text{C}=\text{C}-\text{C}=\text{C} \quad (\text{trans-cis}) \end{array}$	$\left. \begin{array}{l} \text{CD} \quad \quad \text{C} \\   \quad \quad   \\ \text{C}=\text{C}-\text{C}=\text{C} \\ (\text{trans-cis}) \end{array} \right\}$
$\begin{array}{l} \text{C} \quad \quad \text{C} \\   \quad \quad   \\ \text{C}=\text{C}-\text{C}-\text{C} \\    \quad \quad    \end{array}$	
$\begin{array}{l} \text{C} \quad \quad \text{C} \\    \quad \quad    \\ \text{C}-\text{C}-\text{C}-\text{C} \end{array}$	
$\begin{array}{l} \text{C} \quad \quad \text{C} \\   \quad \quad   \\ \text{C}=\text{C}-\text{C}=\text{C} \quad (\text{trans}) \end{array}$	$\left. \begin{array}{l} \text{CD} \quad \quad \text{C} \\   \quad \quad   \\ \text{C}=\text{C}-\text{C}=\text{C} \quad \text{cis} \end{array} \right\}$
$\begin{array}{l} \text{C} \quad \quad \text{C} \\    \quad \quad   \\ \text{C}-\text{C}=\text{C}-\text{C} \end{array}$	
$\begin{array}{l} \text{C} \quad \quad \text{C} \\   \quad \quad   \\ \text{C}=\text{C}-\text{C}=\text{C} \end{array}$	$\begin{array}{l} \text{CD} \quad \quad \text{CD} \\   \quad \quad   \\ \text{C}=\text{C}-\text{C}=\text{C} \end{array}$
	
 ,  , 	

TABLE 4. Polymerization of 1,3-Pentadiene and 2,3-Dimethyl-1,3-butadiene<sup>a</sup>

Monomer	Catalyst	Yield of polymer (%)	Microstructure		
			1,2 (%)	1,4 (%)	3,4 (%)
1,3-Pentadiene	Metallic-K	83	20	80	0
	Pentadienyl-K	82	25	75	0
2,3-Dimethyl-1,3-butadiene	Metallic-K	85	35	65	-
	2,3-Dimethylbutadienyl-K <sub>2</sub>	85	34	66	-

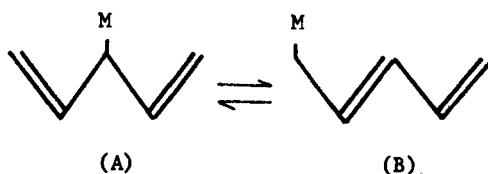
<sup>a</sup>Catalyst, 1 mole % of monomer; solvent, THF; time, 5 days (30°C).

TABLE 5. Relative Mole Ratio of Alkylated Dienes Reacted at C<sub>1</sub> or C<sub>3</sub> of Dienylpotassium Compounds<sup>a</sup>

Potassium compounds	MeI		tert-BuBr	
	C <sub>1</sub> (%)	C <sub>3</sub> (%)	C <sub>1</sub> (%)	C <sub>3</sub> (%)
Pentadienyl-K	65	35	16	84
Hexadienyl-K	44	56	31	69
Cycloheptadienyl-K	12	88	50	50
Cyclooctadienyl-K	5	95	50	50

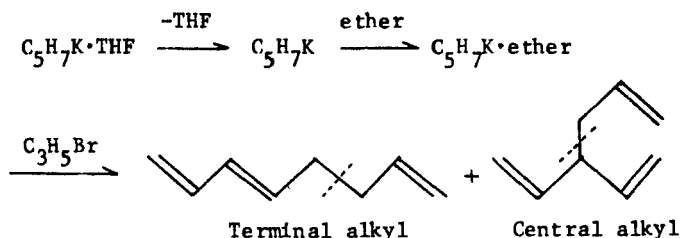
<sup>a</sup> Alkyl halides reacted at C<sub>1</sub> and C<sub>3</sub> of the dienylmetal compounds gave 1,3- and 1,4-type alkylated dienes.

chemical properties of the dienyl metal compounds. Although a 1,4- unconjugated diene was rarely detected in the hydrolyzate of the dienyl metal compounds, both alkylated 1,3- and 1,4-dienes were formed by alkylation (Table 5). The yield of 3-alkyl-1,4-pentadiene increased by increasing the bulkiness of an alkyl halide. The formations of both 1,3- and 1,4-dienes are explained by the existence of an equilibrium between two structures A and B. The correlation existing between the bulkiness of an alkyl halide and the yield of 1,4-dienes



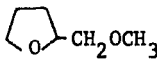
should be interpreted by an electronic factor rather than by the steric factor of an alkyl halide. The pentadienylpotassium tetrahydrofuranate could be converted easily to other etherates by a donor exchange reaction. Ether-free pentadienylpotassium was obtained by heating it at 50°C for 3 hr in vacuum, and addition of ether resulted in the other etherate. The product was isolated as a crystalline etherate. By taking advantage of this reaction, the

solvent effect on the alkylation of pentadienylpotassium was examined by using allylbromide as an alkyl halide. Alkylation occurred mainly at a terminal position to give 1,3,7-octatriene when the reaction occurred in ether. It proceeded only at a central position in *n*-hexane to give 3-allyl-1,4-hexadiene. It is interesting to note that the



increase in the yield of *trans*-1,3-pentadiene by hydrolysis corresponds well to the increase in the yield of dienes alkylated at a central carbon atom (Table 6). These results are reasonably explained by the existence of an equilibrium between the two extreme structures A and B.

TABLE 6. Effect of Coordinated Ether on the Alkylation and Hydrolysis of Pentadienylpotassium

Ethers	Alkylation at		Hydrolyzed pentadiene	
	C <sub>1</sub> (%)	C <sub>3</sub> (%)	cis (%)	trans (%)
Diglyme	89	11	78	22
 CH <sub>2</sub> OCH <sub>3</sub>	87	13	82	18
1,3-Dioxane	85	15	89	11
THF	59	41	38	62
( <i>n</i> -Hexane)	1	99	2	98

STRUCTURES OF THE DIENYL  
METAL COMPOUNDS

Three different planar conformations can be considered for the delocalized structure of pentadienyl anion (I); i.e., U-shaped (cis, cis), W-shaped (trans, trans), and sickle-shaped (cis, trans) [23-25].



U-shaped  
(cis-cis)

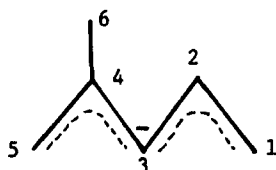


W-shaped  
(trans-trans)

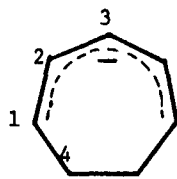


Sickle-shaped  
(trans-cis)

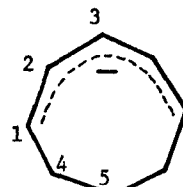
The structure of the pentadienyl alkali metal compound in solution was, therefore, examined by the use of NMR techniques. CMR spectrum of pentadienylsodium, -potassium, and -rubidium showed the presence of only three peaks (Table 7). The sickle-shaped conformation requires five peaks. This result excludes the sickle-shaped structure. PMR spectrum was next studied (Table 8). The proton-proton coupling constant of the inner bond,  $J_{23}$ , is about 11 Hz and corresponds to that of a trans conformation, because the coupling constant  $J_{23}$  in a cis form is known to be about 6.5 Hz and that of a trans one is  $\sim 12$  Hz [19, 26]. The observed coupling constants,  $J_{12}$ , of outer bonds, cis (9.3 Hz) and trans (16.2 Hz), correspond well to those of the known coupling constants of cis (7.5 to 9.0 Hz) and trans ( $\sim 16$  Hz) [26]. Thus pentadienylsodium, -potassium -rubidium, or -cesium is concluded to assume a W-shaped conformation. The conformation of 2-methylpentadienylpotassium (II) is concluded to also be W-shaped. In contrast to this, the conformation of cycloheptadienyl- (III) or cyclooctadienylpotassium (IV) was determined to be U-shaped



II,  $C_6H_9K$



III,  $C_7H_9K$



IV,  $C_8H_{11}K$

TABLE 7. CMR Chemical Shift of Pentadienyl Alkali Metals<sup>a,b</sup>

	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>
I (K)	78.2	135.6	78.5	-	-	-
I' (Na)	77.2	135.5	77.4	-	-	-
I'' (Rb)	76.4	135.0	76.8	-	-	-
II	79.1	133.5	79.7	142.3	76.0	28.5
III	93.5	131.0	75.0	36.8	-	-
IV	88.7	136.1	69.7	29.0	16.0	-

<sup>a</sup>In ppm downfield from external TMS in d<sub>8</sub>-THF (calibrated using the upfield THF peak, assumed to be 25.8 ppm). Data were collected at 25.2 MHz on a Varian XL-100-15 spectrometer with a Digilab Model FTS-NMR-3 Fourier transform accessory.

<sup>b</sup>Peak assignments were made in part from an off-resonance decoupled spectrum, and the data collected at 35°C are shown except for the case of I'(0°).

from the observed value of the coupling constant. This result is in good agreement with the fact that these compounds cannot take a W-shaped conformation due to steric reasons. A general scheme for the initiation reaction of 1,3-pentadiene, 2,4-hexadiene; or other dienes with metallic potassium is reasonably explained by the following equations. As a typical example, the reaction of 1,3-pentadiene with metallic potassium is expressed in the equation. The radical monoanion formed between a diene and metallic potassium couples to give a dianion (Eqs. 1 and 2).

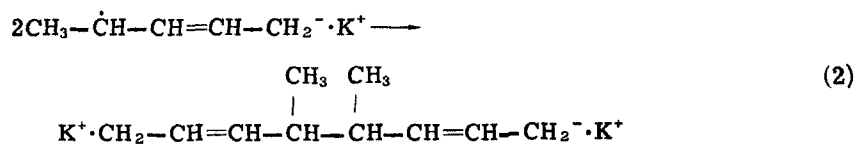


TABLE 8. PMR Chemical Shift of Pentadienyl Alkali Metals<sup>a,b</sup>

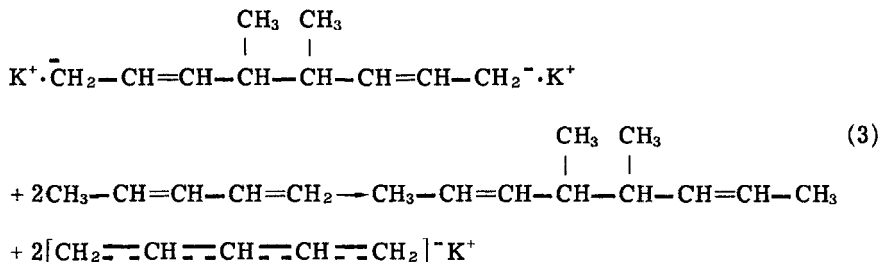
	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	J <sub>12</sub>	J <sub>23</sub>
I (K)	3.45	6.30	3.55	-	-	-	16.2 (trans) 9.3 (cis)	10.9
I' (Na)	3.44	6.29	3.54	-	-	-	16.2 (trans) 9.3 (cis)	10.9
II	3.36	6.23	3.49	-	3.59	1.90	16.4 (trans) 9.5 (cis)	10.6
III	3.84	5.86	3.39	2.72	-	-	8.0 (cis)	7.5
IV	3.08	5.87	2.64	3.10	1.11	-	7.8 (cis)	6.8

<sup>a</sup>In ppm downfield from external TMS in d<sub>6</sub>-THF (calibrated using the upfield THF peak, assumed to be 1.85 ppm).

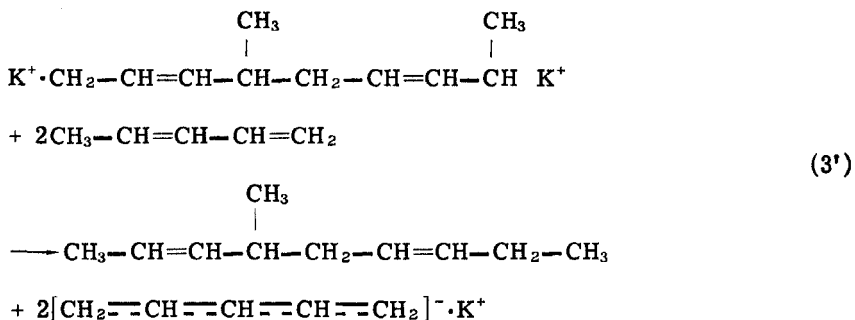
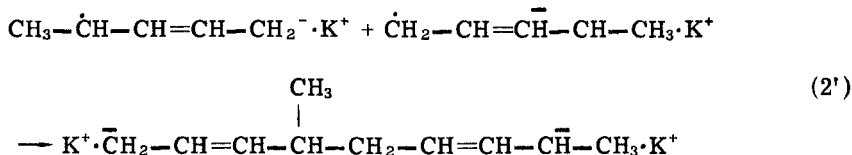
<sup>b</sup>Data were collected at 100.0 MHz on a Varian XL-100-15 spectrometer at 35°C.



The dianion rapidly abstracts two hydrogen atoms from two acidic methyl (or methylene) protons of the two unreacted pentadiene molecules to give 1 mole of reduced dimer and 2 moles of penta-dienylpotassium (Eq. 3).



The rate of reaction in this step is considered to be very fast, because only monodeuterated 1,3-conjugated diene was obtained by deuterolysis. Any deuterated diene dimers were not detected in every case, irrespective of the presence or the absence of a tertiary amine in the reaction system. The formation of other isomeric diene dimer is explained by cross coupling of the isomeric two kinds of radical monoanions (Eq. 2') and then abstraction of allylic proton from 1,3-pentadiene (Eq. 3')

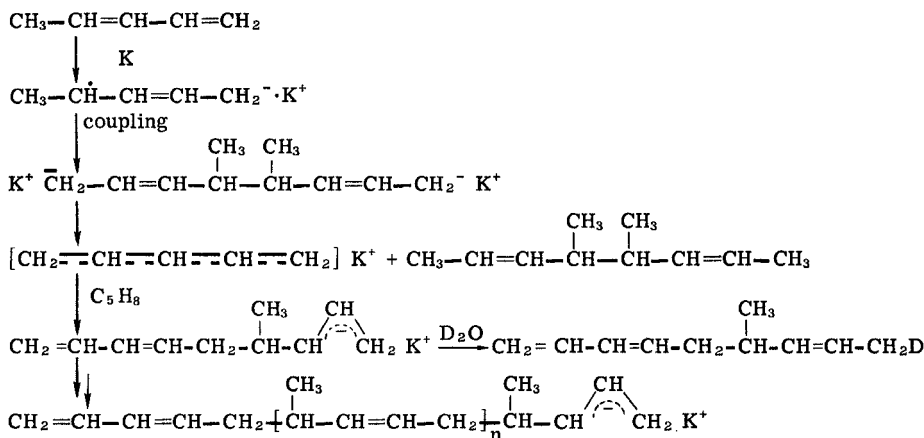


This finding gave us very important information concerning the catalytically active species; i.e., the dienyl monoanion is a real active species. Diene dimer dianion is not necessarily a catalyst species.

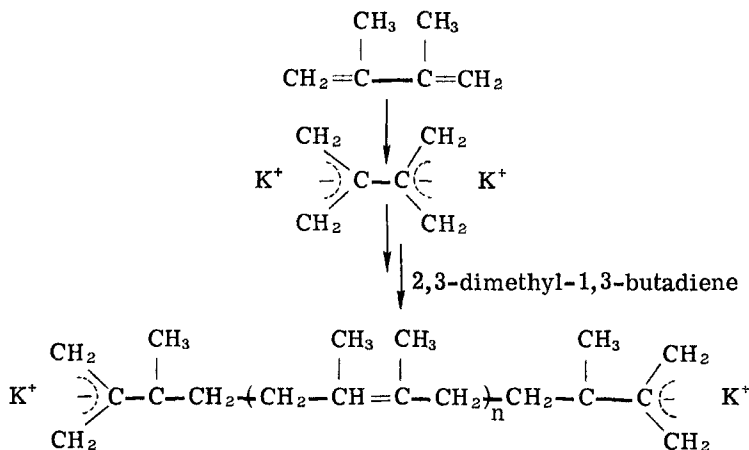
Finally, we should like to turn our attention back to the polymerization of 1,3-pentadiene and 2,3-dimethyl-1,3-butadiene.

The crystalline pentadienylpotassium behaved as a catalyst in the polymerization of 1,3-pentadiene to give results quite similar to those obtained with metallic potassium. This fact seems to suggest that the polymerization of 1,3-pentadiene catalyzed by metallic potassium in the absence of a tertiary amine proceeds via a monoanion as an initiating species. Diene dimer dianions, formed initially as mentioned before, are considered to abstract an allylic proton of the monomer in preference to the initiation of polymerization to give monoanions and reduced diene dimers.

The information about the second step in the polymerization was obtained from the equimolar reaction of 1,3-pentadiene with pentadienylpotassium, which was carried out in tetrahydrofuran at  $-35^{\circ}\text{C}$  for 2 hr. Deuterolysis of this reaction mixture with  $\text{D}_2\text{O}$  gave 6-methyl-1,3,7-nonatriene-9-d, in 20% yield, in addition to poly(1,3-pentadiene). The yield of this pentadiene dimer was about 60% in the case of crystalline pentadienylsodium. In contrast to this, the reaction carried out at  $30^{\circ}$  gave exclusively poly(1,3-pentadiene).



These experimental results suggest that the second step in the polymerization is mainly the 1,4-addition of 1,3-pentadiene to pentadienyl alkali metal, in good agreement with the observed microstructure of poly(1,3-pentadiene), and that the polymerization proceeds via pentadienyl alkali metal with the monoanionic active species. The addition reaction in the polymerization of 2,3-dimethyl-1,3-butadiene with metallic potassium in tetrahydrofuran is considered to be the formation of its dipotassium compound, and the polymerization is considered to proceed via dienyldipotassium compound on both sides with its dianionic active species [27].



### CONCLUDING REMARKS

The number of monoanionic crystalline dienyli alkali metals obtained during the investigation was not only useful for a better understanding of the initiation mechanism but also useful for a general synthesis of other dienyli metal compounds or organic dienyli derivatives. For example, thermally unstable dipentadienyl-zincs was, at first time, prepared by the reaction with anhydrous dichlorzinc at low temperature. Thermally stable Sn, Al, and Si compounds were also obtained [28]. By the reaction of those dienyli metal compounds with carbonyl compounds or alkyl halides, new dienyli derivatives became available.

## ACKNOWLEDGMENTS

The authors express their hearty thanks to Dr. A. Yasuhara and Messrs. Y. Ohnuma, A. Kashiwara, M. Narita, and K. Kanemitsuya for their skillful and enthusiastic experimental support throughout this work.

## REFERENCES

- [1] M. Morton, E. E. Bostick, and R. G. Clarke, J. Polym. Sci., **A1**, 475 (1963); M. Morton, E. E. Bostick, and R. A. Livigni, Ibid., 1735 (1963); M. Morton and L. J. Fetters, Ibid., **A2**, 3311 (1964); M. Morton, L. J. Fetters, R. A. Pett, and J. F. Meier, Macromolecules, **3**, 327 (1970).
- [2] S. Bywater and D. J. Worsfold, Can. J. Chem., **40**, 1564 (1962); D. J. Worsfold and S. Bywater, Ibid., **42**, 2884 (1964); S. Bywater, Adv. Polym. Sci., **4**, 66 (1965); S. Bywater and D. J. Worsfold, J. Phys. Chem., **70**, 162 (1966); A. F. Johnson and D. J. Worsfold, J. Polym. Sci., **A3**, 449 (1965); D. J. Worsfold, Ibid., **A1**, 2783 (1967); D. J. Worsfold and S. Bywater, J. Organometal. Chem., **9**, 1 (1967); F. Schué and S. Bywater, Macromolecules, **1**, 328 (1968); S. Bywater, D. J. Worsfold, and Hollingsworth, Ibid., **5**, 389 (1972).
- [3] H. L. Hsieh, J. Polym. Sci., **A3**, 153, 163, 173 (1965); H. L. Hsieh and O. F. Mekinney, J. Polym. Sci., **B**, 843 (1966).
- [4] J. R. Urwin and J. M. Stearne, Eur. Polym. J., **1**, 227 (1965); D. N. Cramond, P. S. Lawry and J. R. Urwin, Ibid., **2**, 107 (1966).
- [5] H. S. Makowski and M. Lynn, J. Macromol. Chem., **1**, 443 (1966).
- [6] R. S. Stearns and L. E. Forman, J. Polym. Sci., **41**, 381 (1959).
- [7] H. Morita and A. V. Tobolsky, J. Amer. Chem. Soc., **79**, 5853 (1957).
- [8] A. W. Langer, Jr., Trans. N. Y. Acad. Sci., **21**, 741 (1965).
- [9] J. N. Hay, J. F. McCabe, and J. C. Robb, J. Chem. Soc., Faraday I, **68**, 1153 (1972).
- [10] Y. Minoura, K. Shiira, and M. Harada, J. Polym. Sci., **A-1**, **6**, 559 (1968).

- [11] M. Levy and M. Szwarc, J. Amer. Chem. Soc., **82**, 521 (1960); S. Khanna, M. Levy, and M. Szwarc, Trans. Faraday Soc., **58**, 747 (1962); E. Ureta, J. Smid, and M. Szwarc, J. Polym. Sci., **A-1**, **4**, 2219 (1966); D. N. Bhattacharyya, C. L. Lee, J. Smia, and M. Szwarc, J. Phys. Chem., **69**, 608 (1965); K. J. Toelle, J. Smid, and M. Szwarc, J. Polym. Sci., **B**, **4**, 1037 (1965).
- [12] A. V. Tobolsky and C. E. Regers, J. Polym. Sci., **40**, 73 (1959).
- [13] F. Schué, Bull. Soc. Chim. Fr., **4**, 980 (1965).
- [14] K. Ziegler, H. Grimm, and R. Willer, Justus Liebigs Ann. Chem., **542**, 90 (1940).
- [15] K. Suga, S. Watanabe, H. Kikuchi, and T. Watanabe, Can. J. Chem., **46**, 2619 (1968).
- [16] A. Vrancken, J. Smid, and M. Szwarc, Trans. Faraday Soc., **58**, 2036 (1962); C. L. Lee, J. Smid, and M. Szwarc, J. Phys. Chem., **66**, 904 (1962).
- [17] R. L. Williams and D. H. Richards, Chem. Commun., **1967**, 414.
- [18] H. Yasuda, T. Narita, and H. Tani, Tetrahedron Lett., **27**, 2443 (1973).
- [19] R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, Ibid., **3**, 199, 205 (1967); R. B. Bates, S. Brenner, W. H. Deines, D. A. McCombs, and D. E. Potter, J. Amer. Chem. Soc., **92**, 6345 (1970); R. B. Bates, L. M. Kroposki, and D. E. Potter, J. Org. Chem., **37**, 560 (1972).
- [20] Allyllithium have been prepared by addition of alkylolithiums to 1,3-dienes. (a) W. H. Glaze and P. C. Jones, Chem. Commun., **1969**, 1434; W. H. Glaze, J. E. Hanicak, M. L. Moore, and J. Chaudhuri, J. Organometal. Chem., **44**, 39 (1972); W. H. Glaze, Hanicak, J. Chaudhuri, M. L. Moore, and D. P. Duncan, Ibid., **51**, 13 (1973). (b) M. Morton, R. K. Sanderson, and R. Sakata, J. Polym. Sci., **B**, **9**, 61 (1971); M. Morton, L. A. Faluo, and L. J. Fetters, J. Polym. Sci., Polym. Lett. Ed., **10**, 561 (1972). (c) A. Ulrich, A. Deluzarche, A. Maillard, F. Schué, and C. Tanieliean, Bull. Soc. Chim. Fr., **1972**, 2460.
- [21] J. Klein, S. Gily, and D. Kost, J. Org. Chem., **35**, 1281 (1970).
- [22] D. Devaprabhakara, C. G. Cardenas, and P. D. Gardner, J. Amer. Chem. Soc., **85**, 1553 (1963).
- [23] N. Bauld, Ibid., **84**, 4347 (1962).
- [24] D. Glass, R. S. Boikes, and S. Winstein, Tetrahedron Lett., **10**, 999 (1966).

- [25] R. Hoffmann and R. A. Olofson, J. Amer. Chem. Soc., 88, 943 (1966).
- [26] W. T. Ford and M. Newcomb, Ibid., 96, 309 (1974).
- [27] H. Yasuda, A. Yasuhara, and H. Tani, Macromolecules, 7, 145 (1974).
- [28] H. Yasuda and H. Tani, 22nd Symposium on Organometallic Chemistry, Kyoto, 1974; H. Yasuda and H. Tani, Tetrahedron Lett., 1, 11 (1975).