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Cationic Polymerization of Alkyl-1,3-butadienes

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ABSTRACT: The polymerizations of 1- and 2-alkyl-1,3-butadienes, including methyl, ethyl, isopropyl, and *tert*-butyl groups as the alkyl group, were carried out using various cationic catalysts in methylene chloride. The polymerization rate using both $SnCl_4$·TCA and WCl_6 decreased with an increase in the bulkiness of the alkyl group in contrast with $AcClO_4$ and BF_3OEt_2. The nature of the polymers obtained by $SnCl_4$·TCA, WCl_6, and BF_3OEt_2 varied from rubberlike to white powder except that oily oligomers of 2-*tert*-butyl-1,3-butadiene formed. The reactions of 1-isopropyl-, 1-*tert*-butyl-, and 2-alkyl-1,3-butadienes with $AcClO_4$ produced only methanol-soluble oligomers. The content of 1,4-structure of poly(1-alkyl-1,3-butadiene)s decreased as the bulkiness of the substituent increased. The NMR spectra of the oligomers obtained by $AcClO_4$ suggested that a proton elimination in the monomer transfer reaction was governed by Saytzeff's rule. The reactivities of 1- and 2-alkyl-1,3-butadienes toward a styryl cation decreased with an increase in the bulkiness of alkyl group.

It has been known that the linear conjugated dienes could be polymerized readily by both Friedel–Crafts catalysts and Lewis acids. However, there is little information available on the cationic polymerization of alkyl-1,3-butadienes compared with other polymerizations, i.e., radical, anionic, and coordination polymerizations, since the side reactions such as cyclization and cross-linking frequently make the information on the polymer structure uncertain.

The authors have already reported studies of the cationic polymerization of monophenyl-1,3-butadienes,[2–5] diphenyl-1,3-butadienes,[6] and methylphenyl-1,3-butadienes[7] that make clear the relationship between the structure and the reactivity of phenyl-1,3-butadienes. The results obtained in the above polymerizations are summarized as follows:

(i) 1-Phenyl-[2] and 2-phenyl-1,3-butadienes[3] are highly reactive monomers, and the former gave polymers predominantly of 3,4-type, whereas the latter polymerized with 1,4-propagation. (ii) About half of the olefinic double bonds of these polymers were consumed by cyclization. The cyclized polymer of 1-phenyl-1,3-butadiene may have a fused cyclohexane ring and that of 2-phenyl-1,3-butadiene may have a hydrophenanthrene structure. (iii) In the cationic polymerization of diphenyl-1,3-butadienes,[6] only oligomers were obtained because of steric hindrance of the phenyl ring. (iv) The relative reactivities of 1-phenyl-1,3-pentadiene and 3-methyl-1-phenyl-1,3-butadiene toward 1-phenyl-1,3-butadiene were analogous to the tendency of β-methyl- and α-methylstyrenes, whereas the reactivity of 1-methyl-2-phenyl-1,3-butadienes has been enhanced 1.6 times compared to that of 2-phenyl-1,3-butadiene, in the $SnCl_4$·TCA–methylene chloride system at −78 °C.[7] (v) Steric hindrance of substituents plays an important role in determining the microstructure of poly(methylphenyl-1,3-butadiene)s. The olefinic double bonds in their polymers were little cyclized on account of the steric interference of substituents.

In this paper, the authors investigated the cationic polymerizabilities of alkyl-1,3-butadienes and the structure of polymers obtained and compared the results with those obtained in the cationic polymerization of phenyl-1,3-butadienes. The cationic polymerization of isoprene has already been studied by using various catalysts such as Ph_3CSbCl_6,[8] $AlR_nX_{3-n}\cdot H_2O$,[9,10] HCl,[9,10] $AlBr_3$,[11] $AlCl_3$,[12,13] $SnCl_4$,[12,13] $TiCl_4$,[12] BF_3,[13] and $SbCl_5$,[12] in connection with synthetic rubber. The total extent of unsaturation of the olefinic double bonds in the polymer was shown to be less than 80%. In the case of butadiene, the total extent of unsaturation of the olefinic double bonds was 17–36%.[14] These facts suggest that poly(alkyl-1,3-butadiene)s will be cyclized to a large extent during polymerizations. This paper deals with the substituent effect of the alkyl group on the reactivity and the polymer structure of 1- and 2-alkyl-1,3-butadienes.

Experimental Section

Materials. 1,3-Pentadiene (trans/cis = 78/22) was obtained by fractional distillation of the commercial isomeric mixture through a spinning-band column, bp 42 °C. Isoprene obtained commercially was purified by distillation over calcium hydride, bp 34 °C. *trans*-1,3-Hexadiene,[15] *trans*-1-isopropyl-1,3-butadiene, *trans*-1-*tert*-butyl-1,3-butadiene,[16] and 2-*tert*-butyl-1,3-butadiene[17] were prepared by the reactions of Grignard reagents with acrolein, crotonaldehyde, and pinacolon, followed by hydrolysis and the subsequent dehydration of the corresponding alcohols, respectively. The boiling points of these monomers were as follows: hexadiene 75–76 °C; 1-isopropylbutadiene 83–85 °C; 1-*tert*-butylbutadiene 93–108 °C; 2-*tert*-butylbutadiene 98–102 °C. 2-Ethyl-1,3-butadiene and 2-isopropyl-1,3-butadiene were synthesized from butylaldehyde and isovaleraldehyde through the corresponding α-alkylacroleins and 2-alkyl-3-acetoxy-1-butenes according to Marvel's method:[18] 2-ethylbutadiene bp 66–68 °C; 2-isopropylbutadiene bp 85–86 °C. These monomers were distilled twice over calcium hydride. 2-Isopropyl-1,3-butadiene was further purified by means of preparative gas chromatography. The purities of the monomers were more than 97% according to gas chromatographic data.

Solvents (methylene chloride and isooctane) and catalysts ($SnCl_4$, WCl_6, acetyl perchlorate ($AcClO_4$), and BF_3OEt_2) were purified by the usual method. Trichloroacetic acid (TCA) was applied as the cocatalyst of $SnCl_4$ without further purification.

Procedures. Polymerization was carried out under a dry nitrogen atmosphere in a Erlenmeyer flask equipped with a three-way cock. The polymerization was initiated by adding the catalyst solution from a syringe into the monomer solution in an Erlenmeyer flask. Concentration of the water in the system was ca. 5×10^{-4} M. After a given time, the homopolymerization was stopped by adding methanol containing a small amount of ammonia, or *sec*-butanol. The precipitated polymer was separated by filtration and dried under reduced pressure. The methanol-soluble oligomer was isolated by evaporation of the solvent under reduced pressure. The polymers and the oligomers were stored under a dry nitrogen atmosphere and specimens for the oxidation of the polymers were preserved in airtight bottles at room temperature. At suitable time intervals, portions of the copolymerization solution were withdrawn by a syringe and the catalyst was killed by methanol or *sec*-butanol. The concentration of residual monomer was determined by gas chromatography. Monomer reactivity ratios were calculated by Ezrielev's method.[19] The equilibrium constant of π-complex between iodine and monomer was determined by means of UV spectra in isooctane at 30 °C. The IR spectrum of the polymer was measured on a KBr disk by a JASCO IR-E spectrophotometer. ^1H NMR spectrum was measured in carbon tetrachloride solution at 60 MHz on a Hitachi R-20B spectrometer.

Results and Discussion

Cationic Homopolymerization of Alkyl-1,3-butadienes. The result of the cationic homopolymerization of various alkyl-1,3-butadienes by four catalysts in methylene chloride is shown in Table I. The catalytic activities of both $SnCl_4\cdot TCA$ and WCl_6 are shown to be quite similar but different from both $AcClO_4$ and BF_3OEt_2 in connection with the substituents of 1- and 2-alkyl-1,3-butadienes.

In the cases of 1,3-pentadiene, 1,3-hexadiene, and isoprene, the steric effect of the alkyl groups is not so important that these monomers were easily polymerized by the catalyst used, whereas the conversion of the monomers which possessed a bulky alkyl group decreased with an increase in the bulkiness of the alkyl group. On the other hand, the conversion of 1-alkyl-1,3-butadienes by $AcClO_4$ and BF_3OEt_2 increased with an increase in the inductive effect of the substituents.

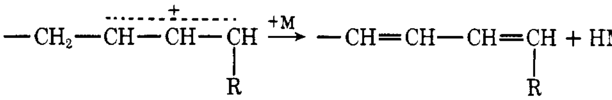
Table I
The Effects of Substituent and Catalyst on the Polymerization Rate of Alkyl-1,3-butadienes[a]

Monomer	Conversion, %			
	$SnCl_4\cdot TCA$	WCl_6	$AcClO_4$	BF_3OEt_2
1,3-Pentadiene	78.5	90.9	15.7	8.6
1,3-Hexadiene	79.7	95.2	35.5	9.6
1-Isopropyl-1,3-butadiene	41.8	44.0	44.2	12.3
1-*tert*-Butyl-1,3-butadiene	32.8	21.7	80.4	21.4
Isoprene	70.3	50.9	94.3	8.3
2-Ethyl-1,3-butadiene	43.6	27.2	81.4	8.7
2-Isopropyl-1,3-butadiene	36.3	21.9	89.6	11.0
2-*tert*-Butyl-1,3-butadiene	29.2	10.2	96.6	14.0

[a] In methylene chloride at 0 °C for 1 h; $[M]_0$ = 0.5 M; $[catalyst]_0$ = 5×10^{-3} M.

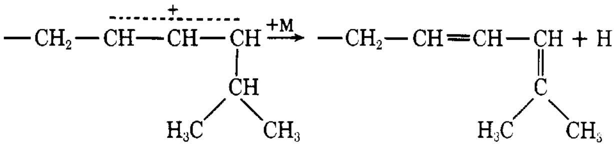
The conversion of 2-alkyl-1,3-butadienes by $SnCl_4\cdot TCA$, WCl_6, and BF_3OEt_2 was less than that of the corresponding 1-alkyl-1,3-butadienes. In the polymerization of 2-alkyl-1,3-butadienes, $AcClO_4$ was shown to be the most effective catalyst with regard to the conversion, but only oligomers were obtained.

The nature of polymers obtained by $SnCl_4\cdot TCA$, WCl_6, and BF_3OEt_2 varied from rubberlike to white powder except that oily oligomers of 2-*tert*-butyl-1,3-butadiene were obtained. The reactions of 1-isopropyl-, 1-*tert*-butyl-, and 2-alkyl-1,3-butadienes with $AcClO_4$ produced only methanol-soluble oligomers. The number-average molecular weights of oligomers of 1- and 2-*tert*-butyl-1,3-butadienes were 450 and 290, respectively. Therefore, a monomer chain transfer reaction was suggested to occur frequently in these systems. In the polymerization of 1-alkyl-1,3-butadienes by $AcClO_4$, the monomer chain transfer may proceed by proton transfer resulting in a change of the propagating end from allylic cation to butadiene type as shown in the following scheme:



$$-CH_2-CH\overset{+}{-}CH-\underset{R}{CH} \xrightarrow{+M} -CH=CH-CH=\underset{R}{CH} + HM^+ \quad (1)$$

R = CH_3, $C(CH_3)_3$



$$-CH_2-CH\overset{+}{-}CH-\underset{CH(CH_3)_2}{CH} \xrightarrow{+M} -CH_2-CH=CH-\underset{C(CH_3)_2}{\overset{}{CH}} + HM^+ \quad (2)$$

R = CH_2CH_3, $CH(CH_3)_2$

This proton transfer reaction was enhanced as the bulkiness of alkyl group interfered with the propagation.

In the case of the polymerization of 2-alkyl-1,3-butadienes using $AcClO_4$, even the oligomer of isoprene could be easily produced. Therefore, the frequency of monomer chain transfer will depend on the charge distribution of propagating end as well as on the steric hindrance of the incoming monomer. The polarization of allylic cation by the alkyl group may decrease the electron density of hydrogen of the neighboring methylene group, and consequently, even the isoprene propagating end favors the release of the proton.

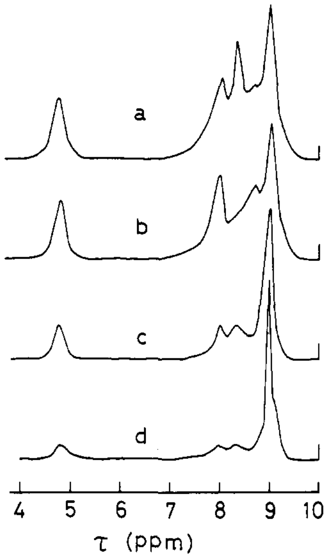
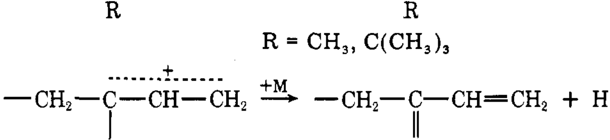
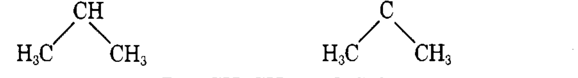


Figure 1. The NMR spectra of poly(1-alkyl-1,3-butadiene)s prepared by using $SnCl_4$·TCA in methylene chloride at 0 °C: (a) poly(1,3-pentadiene); (b) poly(1,3-hexadiene); (c) poly(1-isopropyl-1,3-butadiene); (d) poly(1-*tert*-butyl-1,3-butadiene).



$$—CH_2—\overset{R}{C}—\overset{+}{CH}—CH_2 \xrightarrow{+M} —CH{=}\overset{R}{C}—CH{=}CH_2 + HM^+ \qquad (3)$$

R = CH_3, $C(CH_3)_3$



$$—CH_2—\underset{CH(CH_3)_2}{C}—\overset{+}{CH}—CH_2 \xrightarrow{+M} —CH_2—\underset{C(CH_3)_2}{\overset{\|}{C}}—CH{=}CH_2 + HM^+ \qquad (4)$$

R = CH_2CH_3, $CH(CH_3)_2$

In the cationic polymerization of styrene by $AcClO_4$, the linear dimer was selectively obtained under suitable conditions.[20]

Microstructures of Polymer and Oligomer of Alkyl-1,3-butadienes. The microstructures of the polymers prepared by various catalysts were analyzed by IR and NMR spectroscopies. In the IR spectra of poly(1-alkyl-1,3-butadiene)s, a strong absorption band at 970 cm^{-1} due to trans-1,2-disubstituted ethylenes was observed, whereas none of the absorption bands at 990 and 910 cm^{-1} characteristic of terminal vinyl group were observed.

Representative NMR spectra of the polymers are shown in Figures 1 and 2. The ratios of the peak area of the olefinic protons to that of the total protons were smaller than the theoretical values in all cases. This fact suggests that the olefinic double bonds of the polymers were consumed to some extent, for instance, ca. 48% in the case of poly(1,3-pentadiene), by cyclization or transfer reaction during the polymerization under the present conditions. This side reaction has made the analysis of the polymer structure complicated.

In the NMR spectra of poly(1,3-pentadiene), the allylic methyl proton signals indicated the presence of a 1,2-structure, and the saturated methyl proton signals based on a 1,4-structure and a saturation unit of the cyclized polymer appeared at τ 8.3 and 9.1 ppm, respectively. The peak at τ 8.0 ppm was assigned to both allylic methylene and methyne proton signals. The proton signals for the saturated methylene group in the 1,2-structure should appear around τ 8.7 ppm but the peak was made obscure by overlapping with two strong methyl proton signals. The proton signals for the saturated methylene and methyne groups formed by cyclization and cross-linking reaction seem to appear around τ 8.5 ppm, from the analogy to the NMR spectrum of poly(1-phenyl-1,3-butadiene) prepared in our laboratory.[2] The microstructure of poly(1,3-pentadiene), calculated on the basis of the above assignment, is listed together with the results of the other poly(1,3-alkyl-1,3-butadiene)s in Table II. The microstructure of poly(1,3-hexadiene) could not be determined by NMR spectroscopy since the environment of the proton of a 1,2-structure is similar to that of a 1,4-structure. The microstructures of poly(1-isopropyl-1,3-butadiene) and poly(1-*tert*-butyl-1,3-butadiene) were also calculated in analogy with poly(1,3-pentadiene).

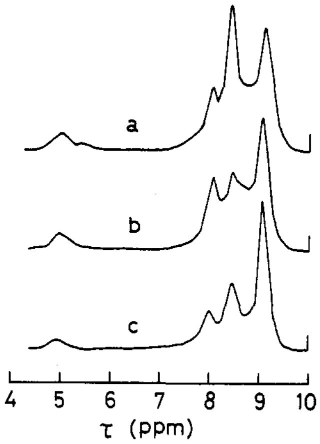


Figure 2. The NMR spectra of poly(2-alkyl-1,3-butadiene)s prepared by using $SnCl_4$·TCA in methylene chloride at 0 °C: (a) poly(isoprene); (b) poly(2-ethyl-1,3-butadiene); (c) poly(2-isopropyl-1,3-butadiene).

Since benzene-soluble polymers were obtained by these catalysts, the consumption of the olefinic double bonds of the polymers might be ascribed mainly to cyclization to saturated bonds. However, the relative ratio of cyclization of the 3,4-structure to that of the 1,4-structure could not be determined. As described in the previous paper,[2] the cyclization of the 3,4-pendent double bonds of poly(1-phenyl-1,3-butadiene) might have proceeded easily to form a ladder polymer having fused cyclohexane rings. In the case of poly(alkyl-1,3-butadiene), however, the stability of the polymer cation produced in the reaction of the 3,4-structure of polymers with propagating species would be the same as that produced from the 1,4-structure. Therefore, the cyclization was reluctantly neglected in the following discussion concerning the microstructures of poly(1-alkyl-1,3-butadiene)s.

The ratio of 1,4-structure/1,2-structure was 1.5 for the polymer obtained in the cationic polymerization of 1,3-pentadiene by $SnCl_4$·TCA in methylene chloride at 0 °C. The ratio of 1,4-adduct/1,2-adduct was 64.5/35 in bromination[21] of *trans*-1,3-pentadiene in carbon tetrachloride at −15 °C and 20/68 in the addition of *p*-chlorobenzenesulfenyl chloride[22] to *trans*-1,3-pentadiene in carbon tetrachloride at 0 °C. Therefore, the orientation of addition in the cationic polymerization of 1,3-pentadiene is shown to be intermediate between that in bromination and in sulfenyl chloride addition.

The 1,4-propagation decreased as the bulkiness of the substituent increased in the case of cationic polymerization of 1-alkyl-1,3-butadienes. As the electron density of the carbon linked with the alkyl group is considered to be the smallest in the propagating allylic cation because of the polarization of alkyl group, the decrease of the 1,4-propagation suggests that the steric effect of alkyl group surpasses the electronic effect.

In the IR spectra of poly(2-ethyl-1,3-butadiene) and

Table II
Microstructure of Poly(alkyl-1,3-butadiene)[a]

Monomer	Catalyst	Microstructure, % Trans-1,4	Trans-1,2	Trans-3,4	Loss of unsaturation
1,3-Pentadiene	$SnCl_4$·TCA	31	21	0	48
1,3-Pentadiene	WCl_6	30	16	0	54
1-Isopropyl-1,3-butadiene	$SnCl_4$·TCA	26	0	44	30
1-*tert*-Butyl-1,3-butadiene	$SnCl_4$·TCA	21	0	52	27
Isoprene	$SnCl_4$·TCA	33	0	0	67
Isoprene	WCl_6	25	0	0	75
2-Ethyl-1,3-butadiene	$SnCl_4$·TCA	34	0	0	66
2-Ethyl-1,3-butadiene	WCl_6	41	0	0	59
2-Isopropyl-1,3-butadiene	$SnCl_4$·TCA	40	0	0	60

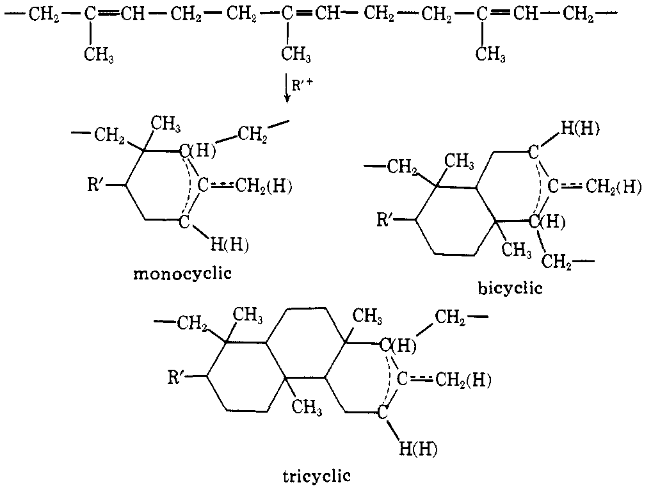
[a] Solvent, methylene chloride; temperature, 0 °C; time, 1 h. The microstructure of poly(1,3-hexadiene) could not be determined by NMR spectroscopy. The consumptions of olefinic double bonds of poly(1,3-hexadiene) prepared by $SnCl_4$·TCA and WCl_6 were 35 and 36%, respectively.

poly(2-isopropyl-1,3-butadiene), a weak absorption band in the range of 860–830 cm^{-1} due to out-of-plane deformation of trisubstituted ethylenes was observed but the peak was much smaller than that of the 1,4-polymer prepared by an anionic initiator, whereas none of the absorption bands at 990, 910, and 890 cm^{-1} characteristic of terminal vinyl and vinylidene groups were observed. The IR spectra of poly(isoprene) indicated the presence of a *trans*-1,4-structure having an absorption band[23] at 1385 cm^{-1} and a small quantity of vinylidene group.

The NMR spectra of poly(2-alkyl-1,3-butadiene)s prepared by $SnCl_4$·TCA are shown in Figure 2. The facts that the degree of unsaturation was less than 50% of the theoretical one and the ratio of the peak area of saturated alkyl proton signals to that of total proton signals was larger than the theoretical one suggest the presence of a cyclized polymer.

In the NMR spectra of poly(isoprene), the olefinic proton signals at τ 4.5–5.2 ppm and τ 5.2–5.6 ppm were due to the 1,4-structure and the 3,4-structure, respectively. Three peaks at 8.1, 8.4, and 9.1 ppm were assigned to the allylic methylene protons, the allylic methyl protons, and the saturated methyl protons, respectively. A strong peak of the saturated methyl proton signals suggests the presence of a large amount of the cyclized poly(isoprene) since the bulk of the polymer obtained was soluble in benzene.

Numerous papers concerning the cycization of natural and synthetic rubbers by $TiCl_4$,[24,25] $SnCl_4$,[26] H_2SO_4,[27] and *p*-toluenesulfonic acid[25] have already been reported. Especially, Agnihotri et al.[25] have followed the progress of cyclization of synthetic *cis*-1,4-poly(isoprene) with $TiCl_4$ and *p*-toluenesulfonic acid by IR and NMR spectroscopies. They reported that the vinylidene proton signals at τ 5.4 ppm first increased with an increase in the cyclicity and then finally almost completely disappeared with a high cyclicity ratio. An average cyclicity of our poly(isoprene) was not a polycyclic structure but a monocyclic or dicyclic one on the basis of 67% loss in unsaturation and by the comparison of the present NMR spectrum with that reported by Agnihotri, et al. Therefore, it is not strange that the partly cyclized poly(1,4-isoprene) has a small amount of vinylidene group.



How the tertiary carbonium ion formed in the process of cyclization behaves will be classified into two cases. In the first case the attack of the carbonium ion on an olefinic double bond of the polymer or monomer will take place. In the second case an abstraction of a proton from the methyne, methylene, or methyl group adjacent to the tertiary carbonium ion will be proposed. In the case of poly(isoprene), the release of a proton from the methyl group will produce a vinylidene group. The fact that the IR and NMR spectra of poly(2-ethyl-1,3-butadiene) and poly(2-isopropyl-1,3-butadiene) showed the absence of vinylidene group will support the assumption that the vinylidene group in poly(isoprene) was produced during cyclization. The cyclization of poly(2-ethyl-1,3-butadiene) and poly(2-isopropyl-1,3-butadiene) may be discussed in the same way as above. The degree of cyclization of poly(2-alkyl-1,3-butadiene) was shown to be greater than that of the corresponding poly(1-alkyl-1,3-butadiene).

The fact that these polymers except poly(1-*tert*-butyl-1,3-butadiene) have gradually aged can be seen from the observations that the white powdery polymers changed into yellow brittle ones and that the transparent rubberlike polymers or oligomers turned yellow or brown. In the IR spectra of the aged polymers, an absorption band at 1715 cm^{-1} due to the characteristics of a carbonyl group appeared. The oxidation rate of poly(2-alkyl-1,3-butadiene) was seen to be much greater than that of poly(1-alkyl-1,3-butadiene). In the case of poly(1-*tert*-butyl-1,3-butadiene) even after storage in an airtight bottle for 1 year at room temperature, no carbonyl group was shown in the polymer by IR spectrum as is similar to the case of poly(phenyl-1,3-butadiene). Field et al. have already described the oxidation of the polymers of linear conjugated dienes such as 1,3-butadiene, isoprene, and chloroprene.[28]

The structure of products obtained by the reaction of alkyl-1,3-butadienes with $AcClO_4$ was investigated. After the reaction mixtures were evaporated, they were analyzed by NMR spectra. Figure 3 shows the NMR spectra of oligomers of alkyl-1,3-butadienes prepared by $AcClO_4$. A strong peak assigned to allylic methyl protons was shown in the NMR

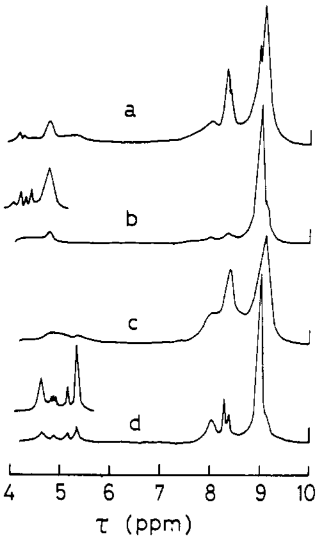


Figure 3. The NMR spectra of oligomers obtained by the reactions of alkyl-1,3-butadienes with $AcClO_4$ in methylene chloride at 0 °C: (a) 1-isopropyl-1,3-butadiene oligomer; (b) 1-*tert*-butyl-1,3-butadiene oligomer; (c) 2-isopropyl-1,3-butadiene oligomer; (d) 2-*tert*-butyl-1,3-butadiene oligomer.

spectra of the oligomers of 2-ethyl-1,3-butadiene and 1- and 2-isopropyl-1,3-butadienes. The ratios of the peak area of the allylic methyl protons to that of the saturated methyl protons were about 1/5, 1/5, and 1/3, respectively. The presence of the allylic methyl group suggests that an α-hydrogen of the alkyl substituents was eliminated as a proton in the transfer reaction of the tertiary carbonium ion of propagating end. The proton transfer of 2-isopropyl-1,3-butadiene is shown in reaction 4. A promotion of the above reaction in the oligomerization of 2-isopropyl-1,3-butadiene using $AcClO_4$ in comparison with that of 2-ethyl-1,3-butadiene can be explained in terms of the Saytzeff's rule of elimination.

The isoprene oligomer had the 1,4-structure of 25% of original unsaturation as the case of the microstructure of poly(isoprene) obtained by using WCl_6. From the NMR spectrum of the oligomer of 1-*tert*-butyl-1,3-butadiene, the ratios of the peak areas of the olefinic, methyne–methylene, and methyl proton signals were calculated as 1.3:3.0:9.7. Therefore, the loss of the olefinic double bonds suggests that some part of the cyclic structure will be present even in the oligomer. Furthermore, the fact that the ratio of the peak area of the methyl protons to that of the total protons was more than 9/14, that is the theoretical value of the 1,4- or 3,4-structure, indicates the presence of a methyl group formed by the proton transfer.

Three kinds of the olefinic proton signals were visible in the NMR spectrum of the oligomer of 2-*tert*-butyl-1,3-butadiene. A peak at τ 4.5–4.8 ppm can be assigned to the olefinic proton signals of the 1,4-structure. Other peaks at τ 4.8–5.2 ppm and τ 5.2–5.4 ppm can be assigned to vinyl and vinylidene proton signals, respectively. The ratio of the peak area of the total olefinic proton signals to that of the total proton signals was 1.1/14. According to the assignment of three kinds of olefinic proton signals, the olefinic double bonds of the oligomers are shown to be composed of trisubstituted ethylenes 45%, vinyl group 28%, and vinylidene group 27%. As the number-average degree of oligomerization of 2-*tert*-butyl-1,3-butadiene oligomer was 3, these vinyl and vinylidene groups may not be ascribed to the presence of 1,2- or 3,4-structure but must be assigned to the terminal unit in the oligomer. If the above assumption is correct, the ratio of 1,4-addition/4,1-addition will be 0.7. Therefore, 4,1-addition will be increased as the bulkiness of alkyl substituent increases in the cationic polymerization of 2-alkyl-1,3-butadienes.

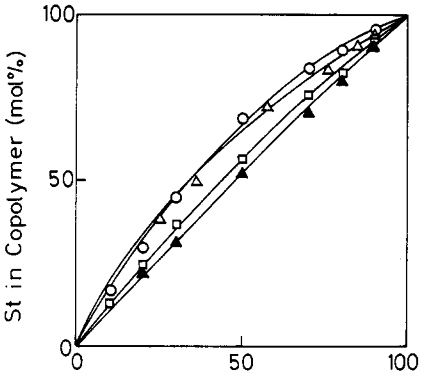


Figure 4. Copolymerization of styrene (St) with 1-alkyl-1,3-butadienes using $SnCl_4$·TCA in methylene chloride at −78 °C ($[M]_0$ = 0.5 M): (▲) 1,3-pentadiene; (□) 1,3-hexadiene; (△) 1-isopropyl-1,3-butadiene; (○) 1-*tert*-butyl-1,3-butadiene.

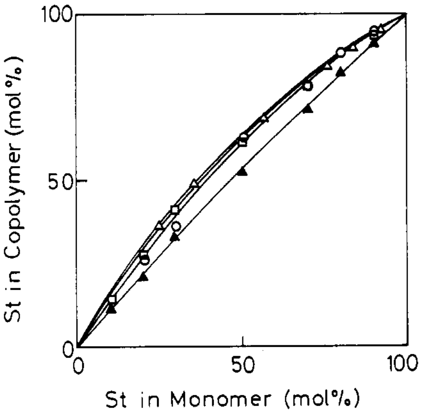


Figure 5. Copolymerization of styrene (St) with 2-alkyl-1,3-butadienes using $SnCl_4$·TCA in methylene chloride at −78 °C ($[M]_0$ = 0.5 M): (▲) isoprene; (□) 2-ethyl-1,3-butadiene, (△) 2-isopropyl-1,3-butadiene; (○) 2-*tert*-butyl-1,3-butadiene.

Copolymerization of Styrene with Alkyl-1,3-butadienes. The copolymerization of styrene with alkylbutadienes was carried out in order to make clear the relative reactivity of alkylbutadienes. Figures 4 and 5 show the copolymer composition curves, and the monomer reactivity ratios are listed in Table III. The reactivity of 1-alkylbutadienes toward a styryl cation was shown to be decreased in the order of methyl > ethyl > isopropyl > *tert*-butyl group.

In the ^{13}C NMR spectra of 1-alkylbutadienes, C-4 carbon signals appeared at 115 ppm downfield from TMS signals regardless of the kind of alkyl group.[29] This finding suggests that the electron densities on C-4 carbon of 1-alkyl-1,3-butadienes in the ground state are almost constant since the inductive effect of alkyl group cannot be transmitted to the carbon of interest. On the other hand, allylic cations formed from 1-alkylbutadienes are stabilized by either the hyperconjugation of methyl group or the inductive effect of alkyl group. As expected from the value of σ^+ of alkyl group, the hyperconjugation of methyl group is superior to the inductive effect of an alkyl group with regard to the stabilization of cation. Therefore, the allylic cation formed from 1,3-pentadiene is more stable than that formed from 1-*tert*-butyl-1,3-butadiene. Furthermore, the considerable steric hindrance of alkyl group must be operative as well as the electronic effect of alkyl group to account for the large difference in reactivity among 1-alkyl-1,3-butadienes.

It has been assumed that the propagation of the cationic polymerization of styrene is subdivided into a separation of counterion by monomer and the subsequent formation of π-complex between the propagating end and the monomer.[30]

Table III
Monomer Reactivity Ratios in Cationic Copolymerizations of Styrene (M_1) with Alkyl-1,3-butadienes (M_2)[a]

M_2	Temp, °C	r_1	r_2	$1/r_1$
1,3-Pentadiene	−78	1.03 ± 0.02	0.90 ± 0.03	0.97
1,3-Hexadiene	−78	1.51 ± 0.05	0.83 ± 0.03	0.66
1,3-Hexadiene	0	0.84 ± 0.03	0.79 ± 0.03	1.19
1-Isopropyl-1,3-butadiene	−78	1.72 ± 0.08	0.50 ± 0.08	0.58
1-*tert*-Butyl-1,3-butadiene	−78	2.42 ± 0.07	0.63 ± 0.03	0.41
1-*tert*-Butyl-1,3-butadiene	0	1.12 ± 0.03	0.95 ± 0.03	0.89
Isoprene	−78	1.13 ± 0.02	0.90 ± 0.02	0.88
Isoprene	0	0.84 ± 0.02	0.89 ± 0.03	1.19
2-Ethyl-1,3-butadiene	−78	1.76 ± 0.04	0.72 ± 0.02	0.57
2-Isopropyl-1,3-butadiene	−78	1.84 ± 0.05	0.62 ± 0.05	0.54
2-*tert*-Butyl-1,3-butadiene	−78	2.02 ± 0.11	0.90 ± 0.09	0.50

[a] $[M]_0$ = 0.5 M; catalyst, $SnCl_4$·TCA; solvent, methylene chloride.

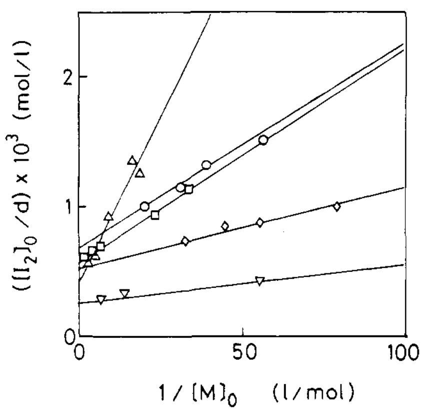


Figure 6. Benesi–Hildebrand's plots for the π-complex between iodine and alkyl-1,3-butadienes in isooctane at 30 °C: (○) 1,3-pentadiene; (□) 1,3-hexadiene; (△) 1-*tert*-butyl-1,3-butadiene; (▽) 2-ethyl-1,3-butadiene; (◇) 2-*tert*-butyl-1,3-butadiene.

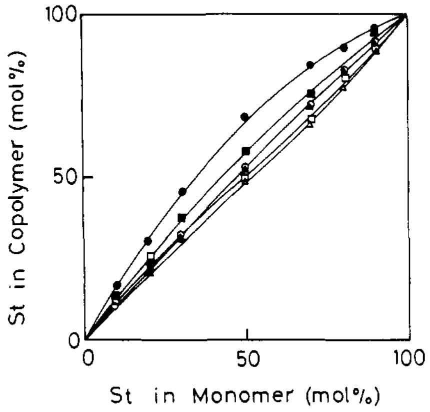


Figure 7. Temperature effect on the copolymerization of styrene (St) with alkyl-1,3-butadienes using $SnCl_4$·TCA in methylene chloride: isoprene (▲) −78 °C, (△) 0 °C; 1,3-hexadiene (■) −78 °C, (□) 0 °C; 1-*tert*-butyl-1,3-butadiene (●) −78 °C, (○) 0 °C.

In order to examine the magnitude of the equilibrium constant of formation of the π-complex between the propagating end and the monomer, iodine was chosen as a model compound of a propagating end. The equilibrium constant between iodine and alkyl-1,3-butadiene was determined in the same manner as described in the previous paper.[7] Figure 6 shows the Benesi–Hildebrand's plots, and the equilibrium constants, K, calculated by the following equation are listed in Table IV.

$$I_2 + M \overset{K}{\rightleftharpoons} I_2 \cdot M \qquad (A)$$

$$[I_2]_0/d = 1/\epsilon + 1/(K\epsilon[M]) \qquad (B)$$

where d, ϵ, K, $[I_2]_0$, and $[M]$ represent the absorbance, the molar extinction coefficient, the equilibrium constant, the initial concentration of iodine, and the monomer concentration, respectively. The formation of π-complex decreased with an increase in the bulkiness of the alkyl group and this order agreed with that of the reactivity of alkyl-1,3-butadiene toward a styryl cation. Therefore, the order of reactivity of 1-alkyl-1,3-butadiene in cationic copolymerization may be explained in terms of the ease of π-complex formation between a styryl cation and 1-alkyl-1,3-butadiene in connection with the steric hindrance of the alkyl group.

In the copolymerization of styrene with 2-alkyl-1,3-butadienes, isoprene was shown to be the most reactive monomer among these 2-alkylbutadienes, but any significant difference of the reactivity among other alkyl-1,3-butadienes, i.e., 2-ethyl-, 2-isopropyl-, and 2-*tert*-butyl-1,3-butadienes, was not observed. Since any 2-alkyl-1,3-butadienes were expected to be capable of the complex formation with iodine to a large extent, this reactivity difference between isoprene and others might be ascribed to the steric interference of the alkyl group with an attacking styryl cation; namely, an attacking path of a styryl cation will be restricted by the bulky substituent of 2-alkyl-1,3-butadiene. Such a steric hindrance of alkyl group which decreases the reactivity was also observed in propylation,[31] mercuration,[32] and bromination[33] of alkylbenzenes and the solvent transfer reaction[34] in the cationic polymerization of styrene.

Table IV
The Equilibrium Constants of π-Complex between Iodine and Alkyl-1,3-butadienes[a]

Monomer	λ, nm	ΣK, l/mol
1,3-Pentadiene	248	43
1,3-Hexadiene	270	34
1-*tert*-Butyl-1,3-butadiene	265	20
2-Ethyl-1,3-butadiene	265	90
2-*tert*-Butyl-1,3-butadiene	256	84

[a] Solvent, isooctane, temperature, 30 °C.

The temperature effect on the copolymerization of styrene (M_1) with alkyl-1,3-butadiene (M_2) was investigated (Figure 7 and Table III). The activation parameters were calculated by using the monomer reactivity ratios in the temperature range from −78 to 0 °C. In order to simplify the terms of the activation parameters, $\Delta H_{11}^{\ddagger} - \Delta H_{12}^{\ddagger}$, $\Delta H_{21}^{\ddagger} - \Delta H_{22}^{\ddagger}$, $\Delta S_{11}^{\ddagger} - \Delta S_{12}^{\ddagger}$, and $\Delta S_{21}^{\ddagger} - \Delta S_{22}^{\ddagger}$ are replaced by using symbols $\Delta H_1^{\ddagger}$, $\Delta H_2^{\ddagger}$, $\Delta S_1^{\ddagger}$, and $\Delta S_2^{\ddagger}$, respectively. The activation parameters calculated were as follows: isoprene (M_2) $\Delta H_1^{\ddagger} = -0.4$ kcal/mol, $\Delta H_2^{\ddagger} = -0.0$ kcal/mol, $\Delta S_1^{\ddagger} = -1.8$ eu, $\Delta S_2^{\ddagger} = 0.2$ eu, hexadiene (M_2) $\Delta H_1^{\ddagger} = -0.8$ kcal/mol,

$\Delta H_2^{\ddagger} = 0.1$ kcal/mol, $\Delta S_1^{\ddagger} = -3.3$ eu, $\Delta S_2^{\ddagger} = 0.7$ eu; 1-*tert*-butylbutadiene (M_2) $\Delta H_1^{\ddagger} = -1.0$ kcal/mol, $\Delta H_2^{\ddagger} = -0.6$ kcal/mol, $\Delta S_1^{\ddagger} = -3.6$ eu, $\Delta S_2^{\ddagger} = -1.9$ eu.

In the case of the attack of styryl cation, the activation enthalpy of addition of alkyl-1,3-butadiene as well as the activation entropy was greater than that of styrene. Therefore, alkyl-1,3-butadienes are shown to be less reactive than styrene in enthalpy term but more reactive than in entropy one, toward a styryl cation. This fact was also observed in the cationic copolymerization of styrene with phenyl-1,3-butadienes.[4,5,7] In the cases of isoprene and hexadiene, however, the activation parameters of alkyl-1,3-butadiene are shown to be similar to but a little less than those of styrene, toward an alkyl-1,3-butadiene propagating end. Consequently, r_1 decreased considerably and r_2 decreased a little as the temperature was raised. Other investigators have reported that the product of the monomer reactivity ratios was abnormally low in the cationic copolymerization of styrene with isoprene at 0 °C and above.[35-37] The tendency to alternation was not observed in our present systems at −78 °C. In the cases of isoprene and 1,3-hexadiene, however, the product of the monomer reactivity ratios seems to decrease as the temperature is raised.

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Anionic Polymerization of the Barium Salt of One-Ended Living Polystyrene. 2. The Effect of Added Barium Tetraphenylboride

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ABSTRACT: Anionic polymerization of barium salt of one-ended living polystyrene (BaS_2) was investigated at ambient temperature in THF in the presence of variable amounts of added barium tetraphenylboride (BaB_2). It was shown that BaB_2 reacts with BaS_2: $BaB_2 + BaS_2 \rightleftarrows 2BaBS$, $K_a = 40$. Ionic dissociation of BaB_2 ($BaB_2 \rightleftarrows BaB^+ + B^-$) in THF was investigated within the temperature range −70 to 20 °C, the results providing the respective Λ_0's and K_{BaB_2}'s. The conductance of $BaS_2 + BaB_2$ in conjunction with the values of the other pertinent equilibria led to $K_b = 3.6 \times 10^{-5}$ for the dissociation, $BaBS \rightleftarrows BaS^+ + B^-$, in THF at 20 °C. This dissociation inhibits the polymerization by suppressing the ionization of BaS_2 forming the propagating S^- ions. The propagation by $(BaS_3)^-$ ions was found to proceed with a rate constant smaller than 100 $M^{-1}\,s^{-1}$. The value of the dissociation constant $BaS_2 \rightleftarrows BaS^+ + S^-$ was reexamined and shown to be 1.1×10^{-10} M rather than 3.7×10^{-10} M reported in the previous study.

In the previous communication[2] we described the kinetics of anionic polymerization of styrene initiated by living polystyrene endowed with one active end and associated with Ba^{2+} counterions. The reaction proceeded at 20 °C in tetrahydrofuran. Conductance data reported in the above paper[2] demonstrated that four distinct species are present in those solutions, namely, $(\sim\!\sim CH_2C^-HPh)_2Ba^{2+}$, $[\sim\!\sim CH_2C^-HPh, Ba^{2+}]^+$, $\sim\!\sim CH_2C^-HPh$, and $[(\sim\!\sim CH_2C^-HPh)_3,Ba^{2+}]^-$, subsequently referred to as BaS_2, $(BaS)^+$, S^-, and $(BaS_3)^-$, respectively.

The reported kinetic data led to the conclusion that the propagation of this polymerization *is due to the free S^- ions*; the contribution of the other species appeared to be negligible. Additional observation strengthened this conclusion. The