Elementary sulfur, evolved during the decomposition of polymer chains by the depolymerization mechanism, contributes to the rapid formation of alkylpolythiolate anions which are reactive during the decomposition reaction and may take part in the formation of disulfide bonds in polymers. Experimentally a negligible increase of elemental sulfur was observed in decomposed polymer samples.

It should be noted here that in the asymmetric decomposition of other polymers, in particular that of poly(propylene oxide), optically active products are also formed.[10]

Taking into consideration the relative facility of the cleavage of polyether in comparison with polythioethers and the fact that, using the catalytic system $ZnEt_2$-2R*OH, asymmetric cleavage of the polymer chains obtained also takes place but to a lesser extent,[10] one can suppose that upon separation of racemic poly(propylene oxide) by the optical active absorbents $ZnEt_2$-(−)R*OH or (+)-borneol, asymmetric destruction of polymer occurred. Because of the absence of data on the molecular weights of initial and fractionated polymers,[13] a supposition can be made that these absorbents react more rapidly with the *l*- (or *d*-) polymer chains, decomposing them to polymers with R*O-Zn-O-··· end groups, which, unlike the free *d*- (or *l*-) polymer chains, are not eluated by *n*-heptane. In our case, when the optically inactive poly(PS) ($[\eta]^{25}$ 1.1 dl/g) was kept for 145 hr in the presence of $ZnEt_2$-2R*OH, an optically active polymer with $[\alpha]^{20}{}_D$ 8.75° and $[\eta]^{25}$ 0.9 dl/g was obtained.

Thus the asymmetric destruction of racemic macromolecules provides new possibilities for the synthesis of optically active polymers and, in addition, it affords low molecular compounds with known optical activity, which is very important for the determination of the efficiency of asymmetric cleavage and the stereospecificity of optically active reagents.

These two processes, selective desulfurization and selective decomposition, are useful additions to the classical methods of separation of racemic compounds used in developing asymmetric syntheses.

Structure and Reactivity in Cationic Polymerization of 2-Alkoxybutadienes

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ABSTRACT: The structure and reactivity in cationic polymerization of 2-alkoxybutadienes were studied. The butadienes used are methoxy-, ethoxy-, isopropoxy-, *tert*-butoxy-, and 2-chloroethoxybutadienes (MOBD, EOBD, IPOBD, tBOBD, and CEOBD, respectively). The four butadienes, except for tBOBD, had a coplanar structure as to diene and *O*-alkyl bond, and the charge on carbon 1 was large. EOBD polymerized fairly rapidly at 0° with several cationic catalysts. The principal products were methanol-soluble oligomer and methanol-insoluble polymer, both of which had 1,4 structure. The relative reactivities of these butadienes were determined from the copolymerizations with ethyl vinyl ether as follows: IPOBD > EOBD > CEOBD > MOBD (>tBOBD).

There have been many investigations on the structure-reactivity relationship in cationic polymerization of alkyl vinyl ethers.[1] One of the characteristics of alkyl vinyl ethers is particularly large reactivity in cationic polymerization owing to the presence of an oxygen adjacent to the vinyl group. On the other hand, many cationic polymerizations of linear conjugated dienes also have been investigated—the cationic polymerizations of butadiene,[2] 2,4-hexadienes,[3] 1- and 2-phenylbutadienes,[4] 1-ethoxybutadiene,[5] and so on. The polymers obtained from these dienes, however, often possess small molecular weights and complex structures.

2-Alkoxybutadiene is regarded as an alkyl vinyl ether as well as a butadiene derivative. For the former case, the α-vinyl group is a substituent; for the latter case, the 2-alkoxy group is a substituent. The importance of each substituent is dependent on the nature of a reaction. Studies on the effect of substituent in such a compound may, therefore, shed light on the nature of a reaction. For instance, Fedor *et al.* have investigated whether 4-methoxy-3-buten-2-one and several 3-alkoxycrotonates are hydrolyzed as a vinyl ether or as a vinyl ketone.[6]

The lone-pair electrons of oxygen in a vinyl ether migrate to the double bond, which makes a vinyl ether basic and reactive in electrophilic reactions. It is interesting to know how this effect is manifested in the molecular properties and cationic polymerizability of 2-alkoxybutadienes. Probably, the coplanarity between diene and an alkoxyl group is affected by increasing the bulkiness of the alkyl group. It is not known how reactive a 2-alkoxybutadiene is in cationic polymerization or whether it produces a high polymer.

In this paper, the molecular structure, properties, cationic polymerizability, and polymer microstructure of several 2-alkoxybutadienes are studied. The results are discussed in comparison with those of alkyl vinyl ethers.

Experimental Section

Materials. Five 2-alkoxybutadienes, that is, 2-methoxybutadiene (MOBD), 2-ethoxybutadiene (EOBD), 2-isopropoxybutadiene (IPOBD), 2-*tert*-butoxybutadiene (tBOBD), and 2-(2-chloroethoxy)butadiene (CEOBD), were prepared by Petrow's method[7]

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(1) See, for example, (a) T. Higashimura, J. Masamoto, and S. Okamura, *Kobunshi Kagaku*, **26**, 702 (1968); (b) H. Yuki, K. Hatada, and M. Takeshita, *J. Polym. Sci., Part A-1*, **7**, 667 (1969); (c) T. Higashimura, T. Masuda, S. Okamura, and T. Yonezawa, *J. Polym. Sci., Part A-1*, **7**, 3129 (1969).

(2) N. G. Gaylord [*Pure Appl. Chem.*, **23**, 305 (1970)] and references therein.

(3) M. Kamachi, K. Matsumura, and S. Murahashi, *Polym. J.*, **1**, 499 (1970).

(4) R. Asami, T. Onoe, and K. Hasegawa, Abstracts, 19th Symposium on Macromolecules, Kyoto, Oct 1970, p 75.

(5) T. Fueno, T. Tsunetsugu, K. Arimoto, and J. Furukawa, *J. Polym. Sci., Part A-1*, **9**, 163 (1971).

(6) (a) L. R. Fedor and J. McLaughlin, *J. Amer. Chem. Soc.*, **91**, 3594 (1969); (b) S. D. Brynes and L. R. Fedor, *J. Amer. Chem. Soc.*, **94**, 7016 (1972).

(7) A. A. Petrow, *Tr. Voronezh. Gos. Univ.*, **8**, 68 (1935); *Chem. Zentralbl.*, 1920 (1937).

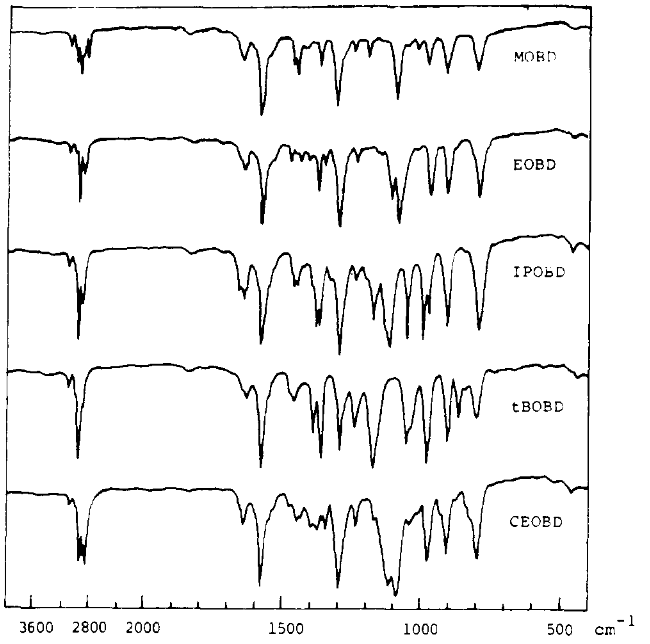
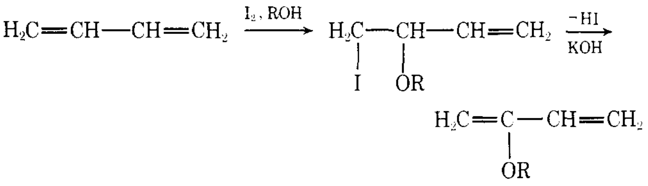


Figure 1. Ir spectra of 2-alkoxybutadienes.

(see Scheme I). Boiling points and refractive indices of the 2-alkoxybutadienes prepared are given in Table I.

Tungsten hexachloride (extra pure) and iodine (E. Merck, resublimed reagent) were used without further purification. Acetyl perchlorate ($AcClO_4$) was synthesized as described elsewhere.[8] Other catalysts (titanium tetrachloride with equimolar trichloroacetic acid ($TiCl_4{\cdot}CCl_3COOH$) and boron trifluoride diethyl etherate (BF_3OEt_2)) and a solvent (toluene) were purified by usual methods.

Scheme I



$$H_2C{=}CH{-}CH{=}CH_2 \xrightarrow{I_2,\ ROH} H_2C(I){-}CH(OR){-}CH{=}CH_2 \xrightarrow[KOH]{-HI} H_2C{=}C(OR){-}CH{=}CH_2$$

Procedures. Uv spectra of the 2-alkoxybutadienes were measured in *n*-hexane (reagent for spectroscopy) on a Shimadzu MPS 50 spectrophotometer. Ir spectra of the dienes were obtained by a Shimadzu IR 27G grating spectrophotometer, using neat samples.

^1H nmr spectra of the 2-alkoxybutadienes were measured in 10 vol % solution in carbon tetrachloride on a Varian HA-100 spectrometer. ^{13}C nmr spectra were measured at 25.14 MHz on a Jeol PFT-100 spectrometer. The spectrum of a neat liquid was taken with accumulation of 100 scans by the Fourier transform method.

Polymerization was performed in an erlenmeyer flask fitted with a three-way cock, under a dry nitrogen atmosphere at $[M]_0 = 1.0M$. Copolymer composition curves were obtained from relative monomer consumption. Monomer consumption was measured by gas chromatography. Monomer reactivity ratios were calculated using the method of Ezrielev *et al.* This was a modified Fineman-Ross method.[9] Ir spectra of polymer samples were measured in KBr disks.

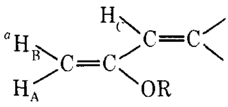
Table I
Boiling Points, Refractive Indices, and Ultraviolet Spectrum Data for 2-Alkoxybutadienes

	Bp, °C (lit.)	n^{20}D (lit. n^{15}D)	λ_{max} (nm)^a
MOBD	75.0 (74.0–75.5)	1.4453 (1.4480)	233
EOBD	94.5 (92.5–93.5)	1.4417 (1.4430)	234
IPOBD	106 (105–107)	1.4400 (1.4410)	237
tBOBD	125	1.4379	234
CEOBD	74 (30 mm)	1.4534	233

^{a} Concentration, 5.00×10^{-5} *M*.

Table II
^1H Chemical Shifts and Spin Coupling Constants of 2-Alkoxybutadienes^a

	Chemical Shift (ppm)					Coupling Constant (cps)		
	τ_A	τ_B	τ_C	τ_D	τ_E	J_{CD}	J_{CE}	J_{DE}
MOBD	5.94	5.97	3.95	4.99	4.52	10.6	17.1	−2.1
EOBD	5.97	5.99	3.95	4.99	4.50	10.5	17.4	−2.2
IPOBD	5.96	5.97	3.98	5.03	4.53	10.5	17.2	−2.3
tBOBD	5.71	5.72	3.97	5.06	4.60	10.3	17.0	−2.3
CEOBD	5.93	5.95	3.93	4.98	4.49	10.5	17.1	−2.2



10 vol %, CCl_4 solution, room temperature.

Theoretical Calculation

MINDO/2 formalism devised by Dewar[10] was used for the theoretical method and parametrizations without further modification. The convergence was judged from the energy level criterion of 1.0×10^{-3} eV in all the orbital energies. The nuclear coordinates used for the 2-alkoxybutadienes and alkyl vinyl ethers are as follows: —C=C— 1.34 Å, =C—O— 1.40, —C—O— 1.43, =C—C= 1.48, =C—H 1.08, —C—H 1.09; ∠C—O—C 110°, ∠C—C—C ∠C—C—O ∠C—C—H 109.5°, ∠C=C—C ∠C=C—O ∠C=C—H 120°. The s-trans conformation of =C—O— bond in alkyl vinyl ethers, and the s-cis of =C—O— bond and s-trans of =C—C= bond in 2-alkoxybutadienes were assumed. Computations were made on a FACOM 230-60 computer at the Data Processing Center of Kyoto University.

Results and Discussion

Molecular Structure and Properties of 2-Alkoxybutadienes. 2-Alkoxybutadienes show a broad absorption in the uv region whose maximum is located in the range of 233–237 nm (see Table I). It is evident in Table I that the absorption shows a small red shift with increasing bulkiness of the alkyl group from methyl to isopropyl. The same trend has been found for alkyl vinyl ethers.[11,12] tBOBD, however, shows an unexpected blue shift, which is quite different from *tert*-butyl vinyl ether. This might be explained in terms of the displanarity between the conjugated double bond and *O*-alkyl bond owing to steric hindrance.

Ir spectra of 2-alkoxybutadienes are shown in Figure 1. Absorptions due to symmetrical stretching vibration of the ether linkage are observed at 1097 cm^{-1} in MOBD, and at 1120 and 1090 cm^{-1} in EOBD, while they are split and shifted in a complex manner in IPOBD and tBOBD. Asymmetrical stretching vibration of the ether linkage in a bulkier alkyl group shows a lower-frequency shift (MOBD 1312 cm^{-1}, tBOBD 1305 cm^{-1}).

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(8) T. Masuda and T. Higashimura, *J. Macromol. Sci.-Chem.*, **5**, 549 (1971).

(9) A. I. Ezrielev, E. L. Brokhina, and E. S. Roskin, *Vysokomol. Soedin., Ser. A*, **11**, 1670 (1969).

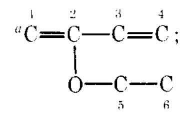
(10) (a) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970); (b) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970).

(11) T. Higashimura, N. Kanoh, T. Yonezawa, K. Fukui, and S. Okamura, *Nippon Kagaku Zasshi*, **81**, 550 (1960).

(12) A. Ledwith and H. J. Woods, *J. Chem. Soc. B*, 310 (1970).

Table III
^{13}C Chemical Shifts of 2-Alkoxybutadienes[a]

	Chemical Shift[b] (ppm)					
	1	2	3	4	5	6
MOBD	86.18	159.61	133.55	113.99	54.34	
EOBD	86.61	158.79	133.89	113.79	62.78	14.44
IPOBD	87.44	157.09	134.57	113.79	68.61	21.67
tBOBD	95.69	155.83	136.61	114.04	77.00	28.56
CEOBD	87.05	158.59	133.60	114.13		

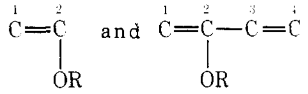
[a] 
$\overset{1}{C}=\overset{2}{C}(-O-\underset{5}{C}-\underset{6}{C})-\overset{3}{C}=\overset{4}{C}$; neat sample, room temperature.

[b] Downfield from tetramethylsilane.

Table IV
Highest Occupied Energy Level and Total Electron Densities of Alkyl Vinyl Ethers and 2-Alkoxybutadienes

	Highest Occupied Level (eV)	Total Electron Density				
		C_1[b]	C_2	C_3	C_4	O
MVE[a]	−9.4744	4.1250	3.6490			6.5173
EVE	−9.4336	4.1271	3.6462			6.5271
IPVE	−9.3092	4.1285	3.6525			6.5264
tBVE	−9.3034	4.1284	3.6585			6.5354
MOBD	−9.0104	4.2073	3.6259	4.0495	3.9810	6.5299
EOBD	−8.9866	4.2082	3.6239	4.0497	3.9815	6.5388
IPOBD	−8.7327	4.2323	3.6198	4.0503	3.9815	6.5476
tBOBD	−8.4450	4.2717	3.6061	4.0522	3.9776	6.5843

[a] MVE, methyl vinyl ether; EVE, ethyl vinyl ether; IPVE, isopropyl vinyl ether; tBVE, *tert*-butyl vinyl ether. [b] Carbons are numbered as follows


$\overset{1}{C}=\overset{2}{C}(OR)$ and $\overset{1}{C}=\overset{2}{C}(OR)-\overset{3}{C}=\overset{4}{C}$

Chemical shifts and coupling constants in the ^1H nmr spectra of 2-alkoxybutadienes are given in Table II. J_{AB} could not be determined, as the chemical shifts of H_A and H_B are very close. As seen from Table II, the chemical shifts of each olefinic proton hardly depend on the kind of alkyl group. However, τ_A and τ_B of tBOBD are exceptionally small as compared with other 2-alkoxybutadienes. This anomaly can also be accounted for by the destruction of the coplanarity between diene and *O*-alkyl bond by steric hindrance.

The ^{13}C chemical shifts of 2-alkoxybutadienes are listed in Table III. Carbon 1 of 2-alkoxybutadienes is highly shielded owing to the large electron density, and the value is very close to that of β carbon in corresponding alkyl vinyl ethers.[13-15] The change in the chemical shift of carbon 1 with the kind of alkyl group is smaller than that of β carbon in alkyl vinyl ethers. The chemical shift of carbon 1 in tBOBD indicates a distinct deshielding in comparison with other 2-alkoxybutadienes. This is also explained in terms of lesser participation of the lone-pair electrons to the conjugation. The resonance peak of carbon 2 appears in low-field region. This is the case also for tBOBD, which implies the predominance of the inductive effect over the resonance effect for the shift of carbon 2.

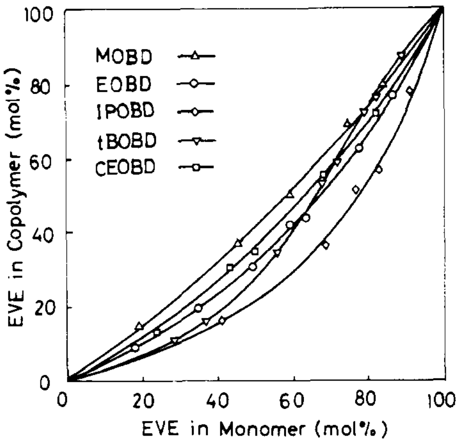


Figure 2. Copolymerizations of ethyl vinyl ether with 2-alkoxybutadienes (−78°, $[M]_0 = 1.0\ M$, BF_3OEt_2, toluene).

The chemical shifts of carbons 3 and 4 are comparatively insensitive to the kind of alkyl group.

The results of molecular orbital calculation of 2-alkoxybutadienes are shown in Table IV. The calculated ionization potentials which are equal to the absolute values of the highest occupied energy level by Koopman's theorem, are smaller than those of alkyl vinyl ethers. The bulkier the alkyl group, the smaller the ionization potential in both classes of compounds. Total electron density on carbon 1 is large in 2-alkoxybutadienes and that on carbon 2 is small. The same trend has been found in alkyl vinyl ethers, but the difference between carbons 1 and 2 is more marked with 2-alkoxybutadienes. The electron density on carbon 1 is large also with tBOBD, which is ascribed to assumption of a coplanar conformation for the molecule. Total electron densities on carbons 1, 2, 3, and 4 tend to be alternating. The electron density increases when the alkoxyl group becomes bulkier.

Reactivity of 2-Alkoxybutadienes in Cationic Polymerization. The cationic homopolymerization of EOBD was carried out using several catalysts (see Table V). Consumption of the monomer was fairly rapid at 0°. It is noteworthy that the reaction rate hardly depends on the kind of catalysts. This seems rather abnormal in the cationic polymerization, and may be attributed to the high stabilization of the formed carbenium ion by the two substituents. Principal polymerization products are a methanol-soluble oligomer and a methanol-insoluble polymer, and the former is preponderant. Under some conditions, cross-linking occurs and a toluene-insoluble fraction is formed. From Table V, the reactivity of EOBD in cationic homopolymerization is considered to be smaller than that of ethyl vinyl ether. For, the latter gives a polymer in a high yield when polymerized for one hour under the same conditions as no. 6 in Table V.

Copolymerizations of 2-alkoxybutadienes with ethyl vinyl ether were attempted in order to know the relative reactivities of 2-alkoxybutadienes. The copolymerizations were performed in toluene by BF_3OEt_2 at −78°, total monomer concentration being 1.0 *M*. The copolymer composition curves and monomer reactivity ratios are given in Figure 2 and Table VI, respectively. The products of r_1 and r_2 in the copolymerizations are approximately unity except for tBOBD. Reciprocal of r_1 increases in the order MOBD < CEOBD < EOBD < IPOBD, which indicates that the reactivity of 2-alkoxybutadienes for the ethyl vinyl ether propagating end increases in this order. This change with the kind of alkyl group is in the same direction as that of alkyl vinyl ethers but the effect of alkyl

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(13) T. Higashimura, S. Okamura, I. Morishima, and T. Yonezawa, *J. Polym. Sci., Part B*, 7, 23 (1969).
(14) K. Hatada, K. Nagata, and H. Yuki, *Bull. Chem. Soc. Jap.*, 43, 3195 (1970).
(15) T. Masuda, *J. Polym. Sci., Part A-1*, in press.

Table V
Cationic Homopolymerizations of EOBD[a]

				Conversion (%)		
No.	Catalyst	Temp (°C)	Time (hr)	Monomer Consumption	MeOH-Soluble Oligomer	MeOH-Insoluble Polymer
1	BF_3OEt_2	0	3	49.2	36.0	2.7
2	$AcClO_4$	0	3	46.3	36.2	5.8
3	I_2	0	3	42.3	30.3	2.6
4	WCl_6	0	3	50.0	33.3	9.1[c]
5	$TiCl_4 \cdot CCl_3COOH$	0	3	53.5	39.1	3.6
6	BF_3OEt_2	−78	24	8.3	nd[b]	3.3
7	$AcClO_4$	−78	24	18.2	nd	3.8
8	I_2	−78	24	13.4	nd	4.2[c]
9	WCl_6	−78	24	7.8	nd	5.4[c]
10	$TiCl_4 \cdot CCl_3COOH$	−78	24	16.9	nd	3.8

[a] $[M]_0 = 1.0\,M$; $[C] = 2.5 \times 10^{-3}\,M$ (0°), $5.0 \times 10^{-3}\,M$ (−78°); toluene. [b] Not determined. [c] A part of the polymer was insoluble in toluene.

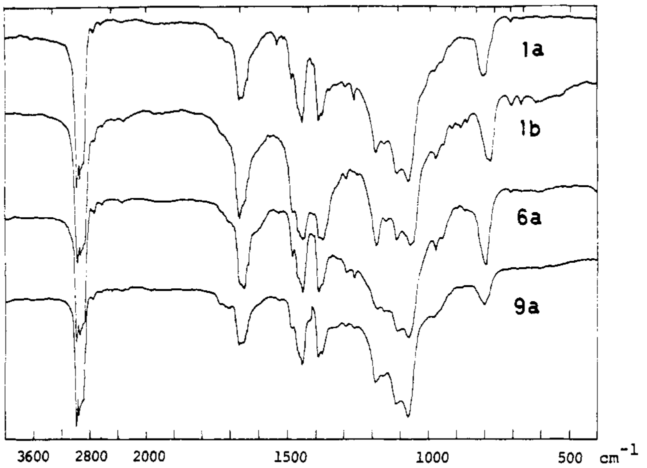

Figure 3. Ir spectra of poly(EOBD). (Numbers refer to those in Table V; a and b designate methanol-insoluble and methanol-soluble parts, respectively.)

group is smaller in 2-alkoxybutadienes[1a,b] (*e.g.*, relative reactivity: MOBD/IPOBD 1.0/2.8; methyl vinyl ether/isopropyl vinyl ether 1.0/11.7). As for tBOBD, $1/r_1$ is peculiarly smaller and $r_1 \times r_2$ is much larger than unity. The result that only tBOBD gives a sigmoidal composition curve may be in close connection with the peculiar properties of tBOBD as shown in Tables I, II, and III. For, a sigmoidal copolymer composition curve has often been found in the cationic copolymerizations of monomers which have a different kind of conjugation and/or basicity.[16] As 2-alkoxybutadienes except tBOBD assume a coplanar structure between diene and *O*-alkyl bond, they may behave similarly to alkyl vinyl ethers. However, the vinyl ether like character of tBOBD is weakened, and in consequence tBOBD will not copolymerize randomly with ethyl vinyl ether. Further studies are necessary for the justification of this reasoning.

Table VI
Monomer Reactivity Ratios for the Copolymerization of Ethyl Vinyl Ether (M_1) with 2-Alkoxybutadienes (M_2)[a]

M_2	r_1	r_2	$r_1 \times r_2$	$1/r_1$
MOBD	0.79 ± 0.06	1.28 ± 0.10	1.01	1.27
EOBD	0.49 ± 0.07	1.92 ± 0.17	0.94	2.04
IPOBD	0.28 ± 0.04	3.38 ± 0.40	0.93	3.57
tBOBD	1.24 ± 0.11	4.70 ± 0.38	5.82	0.81
CEOBD	0.65 ± 0.11	1.96 ± 0.26	1.23	1.54

[a] $[M]_0 = 1.0\,M$, BF_3OEt_2, toluene, −78°.

The order of the reactivity in cationic polymerization, MOBD < CEOBD < EOBD < IPOBD, seems to be intimately correlated to the following orders of molecular properties and structure: conjugation state, MOBD $\simeq$ CEOBD < EOBD < IPOBD; ionization potential, MOBD > EOBD > IPOBD; total electron density on carbon 1, MOBD < EOBD < IPOBD.

The reactivity of EOBD proved to be rather larger than ethyl vinyl ether in copolymerization. Accordingly, it is due to the small reactivity of the EOBD propagating end that EOBD is less reactive than ethyl vinyl ether in homopolymerization.

Microstructure of Poly(EOBD). Poly(EOBD)s show very similar ir spectra to each other regardless of the difference in the molecular weight of the polymers produced and the difference in the temperature or catalyst used for the polymerization (see Figure 3). Stretching vibration of a double bond is observed at 1660 cm^{-1}, and out-of-plane deformation of C—H in trisubstituted ethylene at 800 cm^{-1}. As no absorptions are seen at 990 or 910 cm^{-1}, monosubstituted ethylene does not exist. Therefore, the polymer possesses exclusively 1,4 structure. It is interesting that 1,4 addition proceeds probably owing to steric hindrance though the charge of the propagating cation may be localized mainly on the carbon which has an alkoxyl group. Ethyl α-methylvinyl ether produces a polymer, whereas ethyl α-ethylvinyl ether does not.[17] This difference could be attributed to the difference in steric hindrance. Since the ethyl and the vinyl groups are of similar size, 2-alkoxybutadienes do not seem to polymerize through 1,2-addition mode, which suffers the steric hindrance. The 1,4-addition process due to steric hindrance in spite of the localization of charge on carbon 2 will lead to the slowdown of propagation reactions. This agrees with the inference mentioned in the previous sections on the basis of homo- and copolymerizations.

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(16) See, for example, (a) C. G. Overberger and V. G. Kamath, *J. Amer. Chem. Soc.*, **85**, 446 (1963); (b) T. Masuda, T. Higashimura, and S. Okamura, *Polym. J.*, **1**, 19 (1970).

(17) T. Masuda and T. Higashimura, *Makromol. Chem.*, **167**, 191 (1973).