The Polymerization of Butene Isomers*

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In a previous paper,[1] the effect of the substituents on the radical polymerization of three propenyl chloride isomers, isopropenyl, *trans*-propenyl and *cis*-propenyl chlorides, has been reported. The results obtained may be summarized as follows: 1) All of these isomers homopolymerize with a radical or an ionic initiator only with difficulty, 2) the reactivity of these isomers toward an attack by a polymer radical decreases in the order of isopropenyl$\gg$*trans*-propenyl$\geqq$*cis*-propenyl chloride, and 3) isopropenyl chloride copolymerizes with maleic anhydride easier than other isomers to yield a high-molecular-weight alternate copolymer. These results can be interpreted in terms both of the steric effect and the allylic termination of the substituents in these isomers.

In order to further clarify the effect of the substituents on vinyl polymerization, a study of the polymerization of four butene isomers, *n*-butene-1 (NB), isobutene (IB), *trans*-butene-2 (TB) and *cis*-butene-2 (CB), was taken up and will be reported on the present work. Several studies of the polymerization of butenes have been reported,[2-7] but no detailed study as to the polymerization of the respective butene monomers under similar conditions has been found. The present paper will deal with the effect of the methyl substituents on the polymerization and copolymerization of pure butene monomers in the presence of a radical or an ionic initiator.

Experimental

Materials. — Butene monomers (Matheson Co.) were dried over calcium hydride and then purified by distillation. The physical properties of the butene monomers used in this work are shown in Table I, in which their purities as determined by gas chromatography are also indicated. The gas chromatography of the respective butene isomers was carried out by using an acetonyl-aceton column in a stream of hydrogen (30 ml./min.) at 0°C.

The vinyl acetate (VAC), acrylonitrile (AN), methyl methacrylate (MMA) and maleic anhydride (MAH) used as comonomers were purified by conventional methods.[8] Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. Boron trifluoride-diethyl etherate was used after distillation. Butyllithium (Hans Heinrich Hütte), triethylaluminum (Ethyl Corp.), and titanium trichloride (Staufer Chem. Co.) were used without further purification.

Polymerization Procedure.—In a hard glass tube with a 20-ml. content, the required amount of initiator, solvent and comonomers were placed; this tube was then connected to a vacuum system. After degassing its contents by a repeated freezing and thawing technique, the required amount of butene monomer (which had been weighed beforehand in the vacuum system) was charged into the tube by distillation, and then the tube was sealed off.

In the case of ionic polymerization, a hard glass tube provided with a rubber stopper and from which catalytst had been charged through a syringe, besides a connecting part to vacuum system was used. The polymerization and copolymerization were carried out under shaking in a thermostat maintained at a constant temperature for a given time. After polymerization, the contents of the tube were poured into a large amount of methanol (ether was used in the case of MAH) to precipitate the polymer. The resulting polymer was washed thoroughly, filtered, dried under a vacuum at 40°C, and then weighed. In the case of the polymerization with the Ziegler catalyst, the contents of the tube were poured into a large amount of a hydrochloric acid - isopropyl alcohol mixture to precipitate the polymer, and then the polymer was purified by reprecipitation with isopropyl alcohol from a hot *n*-heptane solution. The rate of conversion was calculated from the weight of the dry polymer obtained.

The composition of the unreacted monomers after cationic or coordinated anionic polymerization was determined by gas chromatography in order to confirm the isomerization of butenes during the polymerization.

The Analysis of the Polymer.—The composition of the resulting polymer was determined by elemental analyses on carbon and hydrogen. The

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* Vinyl Polymerization. CXIII.

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[3] R. L. Meier, *J. Chem. Soc.*, **1950**, 3656.

[4] A. I. Medalia, A. Orzechowski, J. A. Trinchera and J. P. Morley, *J. Polymer Sci.*, **41**, 241 (1959).

[5] J. Gresser and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 3005 (1961).

[6] M. H. Jones and M. P. Thorne, *Can. J. Chem.*, **40**, 1510 (1962).

[7] H. R. Allcock and A. M. Easthana, ibid., **41**, 932 (1963).

[8] E. R. Blout, W. P. Hohenstein and H. Mark, "Monomer," Interscience, New York (1949); T. Otsu and K. Takemoto "Experimental Method of Vinyl Polymerization," Kyoritsu, Tokyo (1960).

TABLE I. PURITIES AND PROPERTIES OF THE BUTENE ISOMERS

Monomer	Purity[a] %	B. p. °C	d	Relative retention volume[b]	Composition of butenes[c]			
					IB	NB	TB	CB
IB	99.27	−6.7	0.674(−49°C)	435	99.7	0.3	0.0	0.0
NB	97.90	−6.3	0.669(−46°C)	405	0.0	100.0	trace	trace
TB	99.35	0.9	0.635(−42°C)	531	trace	0.0	99.7	0.3
CB	99.16	3.6		633	trace	0.0	0.4	99.6

a) Determined by gas chromatography.

b) Relative retention volume of the butenes was calculated taking the retention time of air as unity.

c) Corrected wt. % in the butenes determined by gas chromatography.

structure of the resulting polymers was also checked by means of the infrared spectra of their films, which were made from an ethyl ether or a hot *n*-heptane solution.

The monomer reactivity ratios (r_1 and r_2) were calculated by the Fineman-Ross method.[9]

The Determination of the Chain Transfer Constants of Butene Monomers. — The apparent chain transfer constants (C_m) of butene monomers toward an attack by the polymethyl methacrylate radical were determined at 40, 50 and 60°C. The intrinsic viscosity of the resulting polymer was determined by the viscosity measurement of its dilute chloroform solution at 30°C. The number-average degree of polymerization ($\bar{P}_n$) was then calculated from the intrinsic viscosity, $[\eta]$, according to the following equation:[10]

$$\log \bar{P}_n = 3.261 + 1.256 \log [\eta]$$

Results

The Homopolymerization of Butene Monomers. —The results of the homopolymerization of butene monomers with various initiators are summarized in Table II. These monomers were found not to be polymerized in the presence of AIBN or of *n*-butyllithium.

In the cationic polymerization of the $BF_3 \cdot O(C_2H_5)_2$ catalyst, the reactivities of these monomers were quite low and decreased in the order of IB≫NB>TB—CB. In all cases the resulting polymers were colorless, oily and viscous. The isomerization of the respective butene monomers to the other isomers during the cationic polymerization was not observed, as Table II indicates.

Figure 1 shows the infrared spectra of the resulting polymers, in which the absorption bands characteristic of the sequences of the respective monomer units are observed in their polymers: the absorption bands due to the sequence of the butene-2 unit (1125 cm^{-1}),[11] the ethyl group (766 cm^{-1}),[12] and *gem.*-dimethyl groups (1370, 1389 cm^{-1})[13] were observed in the resulting polymers obtained from butene-2 (TB and CB), NB and IB, respectively.

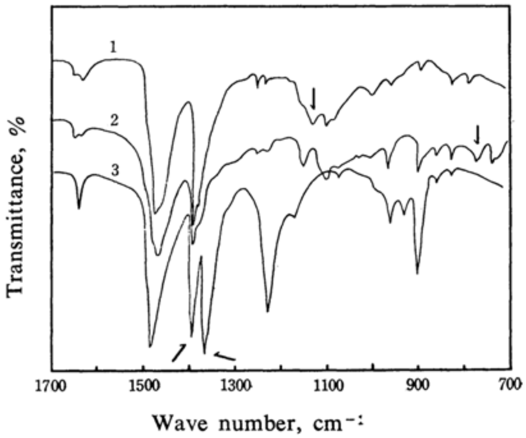

Fig. 1. Infrared spectra of polybutenes obtained with $BF_3 \cdot O(C_2H_5)_2$ (liquid film): (1) poly-*cis*-butene-2, (2) poly-*n*-butene-1, (3) polyisobutene.

In the coordinated anionic polymerization of these butene monomers by the $(C_2H_5)_3Al$-$TiCl_3$ catalyst, as is also shown in Table II, their reactivities were in the order of NB≫CB—TB≫IB. From the results of the composition analyses (Table II) of unreacted butene monomers after the polymerization of IB and NB, the isomerization was not observed in the presence of any catalysts. However, the isomerizations from butene-2 (TB and CB) to NB and from CB to TB (or TB to CB) during the polymerization in the presence of the $(C_2H_5)_3Al$-$TiCl_3$ catalyst were observed.

Figure 2 shows the infrared spectra of these resulting polymers. It was clear that the polymers obtained from IB and NB showed absorption bands due to IB and NB units, respectively, in their infrared spectra. On the other hand, the infrared spectra of the

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9) M. Fineman and S. D. Ross, *J. Polymer Sci.*, **5**, 269 (1950).

10) B. Baysal and A. V. Tobolsky, ibid., **8**, 529 (1952).

11) J. V. Schooten, E. W. Duck and R. Berkenbosch, *Polymer*, **2**, 357 (1961).

12) M. C. Harvey and A. D. Ketley, *J. Appl. Polymer Sci.*, **5**, 247 (1961).

13) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York (1958), p. 24.

TABLE II. RESULTS OF POLYMERIZATION OF BUTENES

Initiation	Monomer	[M] mol./l.	Temp. °C	Time hr.	Yield %	Composition of butenes recovered after polymn.[c) IB	NB	TB	CB
$[AIBN]=1.68\times10^{-2}$ mol./l. in ethyl acetate	IB	2.10	60	20	0	—	—	—	—
	NB	2.09	60	20	0	—	—	—	—
	TB	1.99	60	20	0	—	—	—	—
	CB	1.99	60	20	0	—	—	—	—
$[BF_3\cdot O(C_2H_5)_2]=3.0\times10^{-2}$ mol./l. in bulk	IB[a)	10.00	0	36	5.7	—	—	—	—
	NB[a)	9.99	0	36	0.2	—	—	—	—
	NB	11.93	27—30	240	3	0.0	97.9	0.9	1.2
	TB	11.34	27—30	240	0.5	0.0	0.0	99.8	0.2
	CB	11.34	27—30	240	1	0.0	0.1	1.5	98.4
$[n\text{-}C_4H_9Li]$ 10^{-1} mol./l. in toluene	IB	6.02	−78	41	0	—	—	—	—
	NB	5.97	−78	41	0	—	—	—	—
	TB	5.67	−78	41	0	—	—	—	—
	CB	5.67	−78	41	0	—	—	—	—
$[(C_2H_5)_3Al\text{-}TiCl_3]$[b) in *n*-heptane	IB	5.97	60	12	0.5	100.0	trace	0.0	0.0
	NB	6.03	60	0.83	73.1	0.0	100.0	0.0	0.0
	TB	6.08	60	12	1.0	trace	2.1	97.9	trace
	TB	6.08	80	28	17.5	trace	3.1	65.7	31.2
	CB	5.93	60	12	4.5	trace	2.6	27.1	70.3
	CB	5.93	80	28	18.0	trace	3.5	55.6	40.9

a) $[BF_3\cdot O(C_2H_5)_2]=5.0\times10^{-2}$ mol./l. in toluene

b) $[TiCl_3]=5.0\times10^{-2}$ mol./l., Al/Ti=2.0, Aging of catalyst: 27°C, 1 hr.

c) Corrected wt. % in the recovered butenes determined by gas chromatography

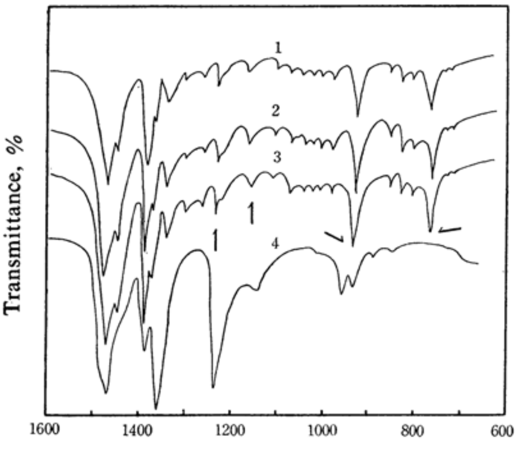

Fig. 2. Infrared spectra of the polymer resulted from *n*-butene-1 (1), *trans*-butene-2 (2), *cis*-butene-2 (3) and isobutene (4) with $(C_2H_5)_3Al\text{-}TiCl_3$ (film).

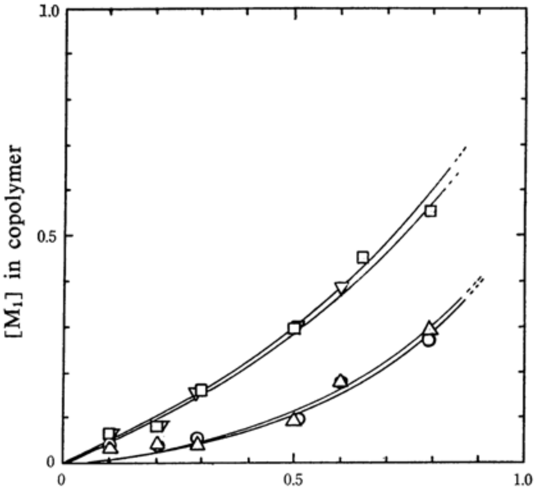

Fig. 3. Monomer-copolymer composition curves for copolymerization of butenes (M_1) with VAC (M_2) initiated by AIBN at 60°C: (□) IB-VAC system; (▽) NB-VAC system; (△) TB-VAC system; (○) CB-VAC system.

polymers from TB and CB showed no absorption bands due to the respective butene-2 units, although the absorption bands at 766 (ethyl group), 925 and 1221 cm⁻¹ (crystal. bands)[12) which are characteristic of the polymer of NB were observed.

Copolymerization with VAC. — The results of the radical copolymerization of butene monomers with VAC initiated by AIBN at 60°C are shown in Table III, in which the rate of copolymerization markedly decreases as the concentration of the butene monomer

TABLE III. RESULTS OF COPOLYMERIZATION OF THE BUTENES WITH VAC, AND AN AT 60°C; [AIBN] $=1.68\times10^{2}$ mol./l. IN BENZENE

Polymerization system	$[M_1]$ in comonomer mol. %	Time hr.	Yield %	Rate of copolymerization %/hr.	Copolymer		
					C %	H %	$[M_1]$ mol. %
IB(M_1)-VAC(M_2)	9.98	2	11.6	5.8	57.11	7.24	6.54
	19.70	3	13.3	4.5	57.41	7.47	8.01
	29.80	4.5	7.1	1.6	59.25	7.95	16.68
	50.21	8	3.4	0.4	62.13	8.60	29.21
	66.17	42	12.9	0.3	66.33	9.29	45.55
	80.17	49	3.0	0.1	69.17	10.15	55.51
NB(M_1)-VAC(M_2)	9.91	2	5.6	2.8	57.12	7.13	6.58
	19.93	3	2.3	1.9	57.61	7.36	8.97
	28.30	4.5	5.5	1.2	59.14	7.79	16.20
	50.00	8	1.2	0.2	62.52	8.59	30.82
	59.97	42	4.6	0.1	64.45	8.95	38.49
	79.70	49	0.9	0.02	—	—	—
TB(M_1)-VAC(M_2)	10.19	2	8.9	4.4	56.48	7.12	3.41
	19.86	3	8.0	2.7	56.59	7.20	3.97
	28.15	4.5	7.1	1.6	56.61	7.25	4.06
	49.89	8	3.8	0.5	57.50	7.38	8.45
	59.86	42	9.2	0.2	59.62	7.85	18.36
	79.09	49	2.4	0.1	62.15	8.40	29.29
CB(M_1)-VAC(M_2)	10.19	2	7.7	3.8	56.51	7.16	3.56
	19.86	3	7.4	2.5	56.44	7.17	3.20
	28.15	4.5	2.5	0.6	56.60	7.20	4.01
	49.89	8	2.3	0.3	57.58	7.48	8.84
	59.86	42	8.2	0.2	59.44	7.80	17.53
	79.09	49	2.4	0.1	61.42	8.49	26.22
IB(M_1)-AN(M_2)	9.90	0.5	1.6	3.1	69.04	6.47	6.10
	19.83	1	1.8	1.8	71.59	7.53	19.91
	29.77	1.3	1.6	1.2	73.14	7.91	28.40
	39.74	2	1.7	0.9	73.81	8.12	32.10
	59.74	4	1.8	0.4	75.06	9.55	39.05
	79.83	21	5.6	0.3	75.62	9.47	42.17
NB(M_1)-AN(M_2)	10.08	0.5	4.7	9.3	67.95	5.86	0.26
	20.20	1	7.4	7.4	68.32	6.26	2.25
	29.60	1.3	3.9	3.0	68.33	6.22	2.30
	39.54	2	2.2	1.1	68.80	6.41	4.82
	59.54	4	2.4	0.6	71.25	7.57	18.05
	79.69	21	4.6	0.2	73.94	8.27	32.83
TB(M_1)-AN(M_2)	9.89	0.5	3.7	7.4	66.94	5.84	0
	19.92	1	3.3	3.3	67.46	6.06	0
	30.09	1.3	2.5	2.0	68.06	6.20	0.85
	40.41	2	2.2	1.1	68.26	6.28	1.92
	59.87	4	1.4	0.3	68.85	6.87	5.08
	78.86	8	0.4	0.1	71.37	8.27	18.71
CB(M_1)-AN(M_2)	9.89	0.5	4.1	8.3	67.05	5.96	0
	19.92	1	4.4	4.4	66.92	5.98	0
	30.09	1.3	1.7	1.3	67.59	6.19	0
	40.41	2	1.9	0.9	67.81	5.93	0
	59.87	4	1.1	0.3	69.21	7.26	7.01
	78.86	21	1.2	0.1	71.11	7.81	17.29

TABLE IV. RESULTS OF COPOLYMERIZATION OF BUTENES (M_1) WITH MAH (M_2) AT 60°C; [AIBN]$=1.68\times10^{-2}$ mol./l. IN BENZENE

M_1	$[M_1]$ in comonomer mol. %	Time hr.	Yield %	Rate of copoly-merization %/hr.	Copolymer			
					C %	H %	$[M_1]$ mol.%	η_{sp}/C[a]
IB	19.87	0.17	6.8	41.0	61.02	6.37	46.05	—
	39.87	0.17	12.2	73.4	61.32	6.47	46.96	1.20
	59.80	0.08	13.9	167	61.35	6.66	47.06	—
	79.69	0.33	4.2	12.7	61.48	6.45	47.44	—
NB	20.07	20	20.4	1.0	61.04	6.37	46.10	—
	39.67	20	27.7	1.4	61.33	6.18	47.72	0.08
	60.05	20	45.5	2.3	61.70	6.24	48.11	—
	80.09	4.3	13.7	3.2	61.81	6.70	48.44	—
TB	19.79	20	7.0	0.4	60.15	6.12	43.33	—
	39.79	20	13.0	0.6	60.85	6.13	45.52	0.06
	59.74	20	14.7	0.7	61.23	6.57	46.68	—
	79.81	4.3	3.2	0.8	61.26	6.24	46.78	—
CB	19.79	20	9.2	0.5	60.34	6.27	43.92	—
	39.79	20	16.9	0.8	60.76	6.12	45.24	0.05
	59.74	20	22.1	1.1	61.16	6.00	46.47	—
	79.81	4.3	5.0	1.2	61.22	6.62	46.65	—

a) Determined by viscosity measurement of 0.4% tetrahydrofuran solution in an Ubbelohde viscometer.

increases. On the basis of the results of Table III, the monomer-copolymer composition curves are shown in Fig. 3.

Copolymerization with AN. — The results of the copolymerization of butene monomers with AN initiated by AIBN are shown in Table III, from which the monomer-copolymer composition curves are shown in Fig. 4.

Copolymerization with MAH. — The results of the copolymerization of the butene monomers with MAH initiated by AIBN at 60°C are shown in Table IV, from which the monomer-copolymer composition curves are shown in Fig. 5. As is clearly indicated in Table IV, the composition of the resulting copolymers was found to be independent of

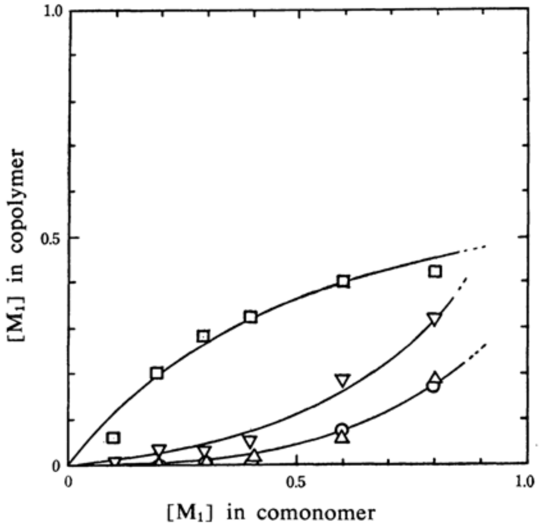

Fig. 4. Monomer-copolymer composition curves for copolymerization of butenes (M_1) with AN (M_2) initiated by AIBN at 60°C: (□) IB-AN system; (▽) NB-AN system; (△) TB-AN system; (○) CB-AN system.

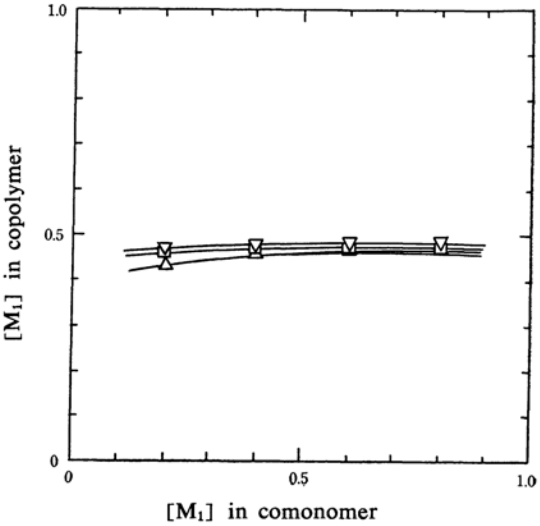

Fig. 5. Monomer-copolymer composition curves for copolymerization of butenes (M_1) with MAH (M_2) initiated by AIBN at 60°C: (□) IB-MAH system; (▽) NB-MAH system; (△) TB-MAH system; (○) CB-MAH system.

TABLE V. MONOMER REACTIVITY RATIOS (r_1, r_2) AND Q_1, e_1 VALUES FOR BUTENES

M_1	M_2	r_1	r_2	$1/r_2$	Relative reactivity	Q_1	e_1
IB	VAC	0.31	2.15	0.47	3.8	0.014	−0.86
IB	AN	0.00	0.80	1.25	17.6	—	—
NB	VAC	0.34	2.0	0.50	4.0	0.012	−0.69
NB	AN	0.10	8.0	0.13	2.0	—	—
TB	VAC	0.07	7.0	0.14	1.1	0.004	−1.06
TB	AN	0.00	14.0	0.07	1.0	—	—
CB	VAC	0.07	8.0	0.13	1.0	0.004	−0.98
CB	AN	0.00	14.0	0.07	1.0	—	—

the monomer feed ratio and to be a 1 : 1 molar composition of MAH and the butene monomer.

IB copolymerized quite readily with MAH to give a colorless polymer which had a relatively high specific viscosity. However, the other butene monomers copolymerized at a rather slow rate, and light yellow-colored copolymers of a lower specific viscosity were obtained. Accordingly, it was clear that the tendency of these butene monomers to alternate copolymerization with MAH decreased in the order of $IB \gg NB \geqq CB \geqq TB$.

The rate of the copolymerization of butene monomers with MAH increased with an increase in the initial concentration of the butene monomer and showed the maximum shown in Fig. 6.

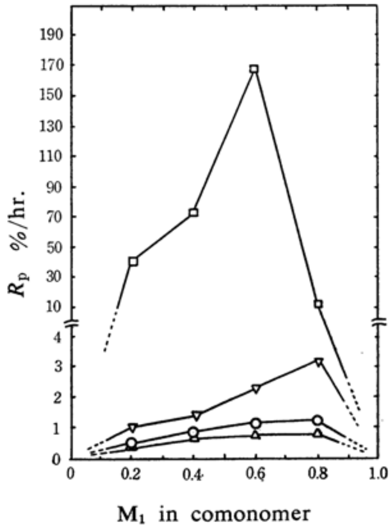

Fig. 6. Relationship between R_p and monomer feed ratio for copolymerization of butenes (M_1) with MAH (M_2) initiated by AIBN at 60°C.

□ Isobutene
▽ *n*-Butene
△ *trans*-Butene
○ *cis*-Butene

The Monomer Reactivity Ratio and the *Q* and *e* Values for Butene Monomers.—The monomer reactivity ratios (r_1 and r_2) were calculated for these copolymerizations according to the Fineman-Ross method.[9] The results are summarized in Table V. From the values of r_1 and r_2 for the copolymerization with VAC, the Q and e values for butene monomers were calculated by assuming that $Q=0.026$ and $e=-0.22$ for VAC.[14]

As may be understood from this table, the values of Q_1 for butene monomers and the values of $1/r_2$ which might indicate the reactivity of butene monomers to polymer radicals were found to have the same tendency in their reactivities to cationic polymerization.

The Chain Transfer Constants of Butene Monomers.—Since it was confirmed from the elemental analyses and the infrared spectra of the resulting polymers that these butene monomers scarcely copolymerized with MMA at all, the apparent chain transfer constant of

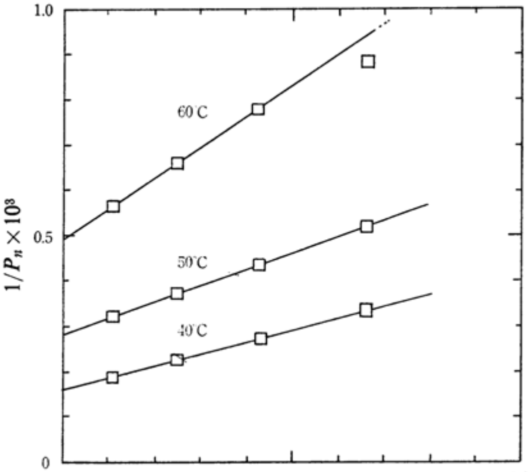

Fig. 7. Relationship between $1/\overline{P}_n$ and IB/MMA for copolymerization of isobutene with MMA.

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[14] L. J. Young, *J. Polymer Sci.*, **54**, 411 (1961).

TABLE VI. RATE CONSTANTS OF BUTENES TOWARD ATTACK OF RADICALS

Butene	k_2/k_1 (65°C)	k_3/k_2 (65°C)	$C_m \times 10^3$		
			(40°C)	(50°C)	(60°C)
IB	35.6	0.06	0.25	0.44	0.69
NB	26.9	0.25	0.31	0.51	0.73
TB	6.9	0.72	0.30	0.52	1.08
CB	3.3	0.95	0.32	0.49	1.12

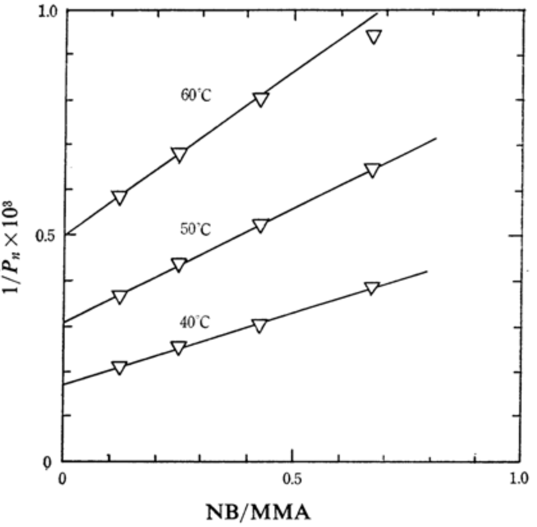

Fig. 8. Relationship between $1/\overline{P}_n$ and NB/MMA for copolymerization of *n*-butene with MMA.

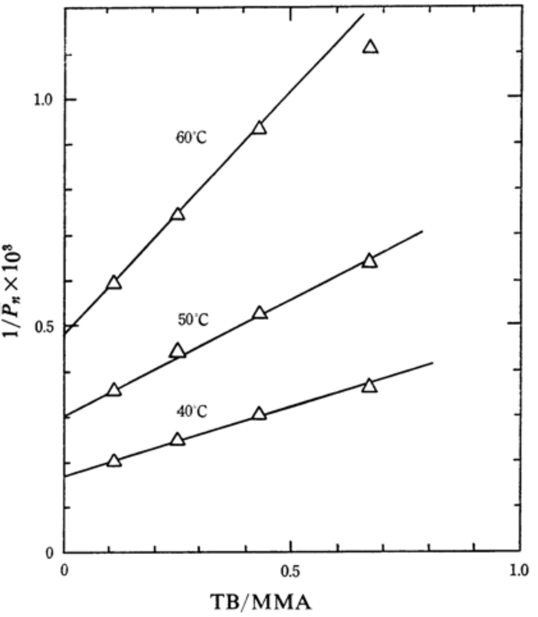

Fig. 9. Relationship between $1/\overline{P}_n$ and TB/MMA for copolymerization of *trans*-butene with MMA.

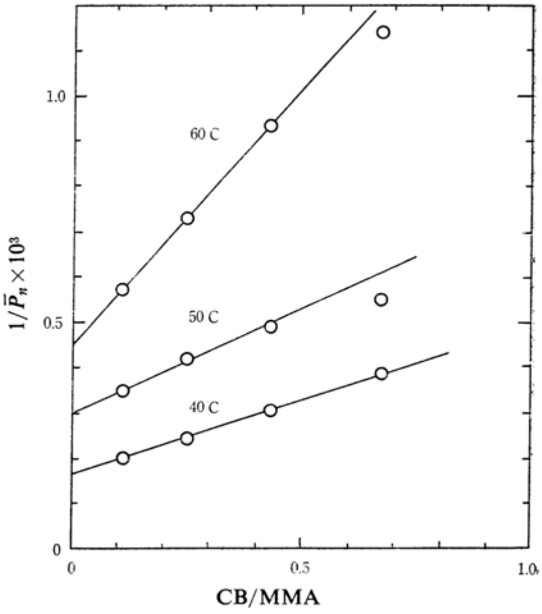

Fig. 10. Relationship between $1/\overline{P}_n$ and CB/MMA for copolymerization of *cis*-butene with MMA.

these butene monomers toward an attack by a polymethyl methacrylate radical were determined. The results are shown in Figs. 7—10 and Table VI.

Table VI also shows the relative reactivities of a methyl radical to butene isomers determined by Szwarc and his co-workers.[15] In this table, k_1, k_2 and k_3 are the rate constants, respectively, for hydrogen abstraction from isooctane, for addition to butenes, and for hydrogen abstraction from butenes toward the attack of a methyl radical.

Discussion

In Tables II and III it was observed that these butene monomers did not homopolymerize in the presence of a radical initiator and that their copolymerization reactivities with VAC were in the order of IB≫NB>TB—CB. The

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[15] R. P. Buckley, F. Leavitt and M. Szwarc, *J. Am. Chem. Soc.*, **78**, 5557 (1956); R. P. Buckley and M. Szwarc, *Proc. Royal Soc.*, **A240**, 396 (1957).

results for butene isomers were almost the same as those for propenyl chloride isomers.[1]

The low reactivitities of butene-2 monomers which are 1, 2-disubstituted ethylene may be understood as the result of an increased steric effect of the substituents. It is also supported by the smaller Q values of TB and CB than those of IB and NB, as Table V shows.

In the copolymerizations of propenyl chloride isomers, it was found that the trans-isomers were about two or three times more reactive than the cis-isomer toward attacks by polymer radicals. However, TB and CB were found to have almost the same reactivity. This result may be interpreted as indicating that CB takes a coplanar structure just like that of TB in the transition state.

From Table IV it is obvious that the tendency of the butene monomers to alternate copolymerization with MAH decreases in the order of IB≫NB>CB≧TB, which is similar to the findings concerning propenyl chloride isomers.[1] This order in the reactivity of butene isomers was also similar to that of their hydrogen abstractions by the methyl radical and the polymethyl methacrylate radical, as is shown in Table VI. Accordingly, it may be concluded that the degradative chain transfer reactivity of butene isomers, which might be determined by their steric effects, is an important factor in their polymerizations and copolymerizations in the presence of a radical initiator.

The rate of the copolymerization of butene or propenyl chloride isomers with MAH markedly decreases with an increase in the concentration of butene or propenyl chloride in the monomer mixture. However, it is interesting that the rates of the copolymerizations of butenes with MAH gave a maximum as a function of the monomer concentration, as is shown in Fig. 6. This result might indicate that the specific stabilization of the transition state in alternating propagation which would lead to an energy-lowering is significant, as has been pointed out by Price[16] and Walling[17].

As can be seen from Table II, no butene monomers could be homopolymerize in the presence of *n*-butyl lithium, and only IB could be homopolymerized by $BF_3 \cdot O(C_2H_5)_2$. Their reactivities for cationic polymerization decreased in the order of IB≫NB>TB—CB, and no isomerization was observed during the polymerization.

As is clearly shown in Table II, however, NB, TB and CB could be easily homopolymerized in the presence of the $(C_2H_5)_3Al\text{-}TiCl_3$ catalyst to give high-molecular-weight polymers. It was noted that TB and CB, which were known[18] not to homopolymerize because of the steric effect, could homopolymerize at rather high temperatures. It was confirmed by infrared spectra and X-ray diffraction analyses that all of the polymers resulting from TB and CB consisted of the NB sequence.

The isomerization from TB to CB or NB and that from CB to TB or NB during the polymerization were observed in the presence of this coordinated catalyst. Accordingly, it was deemed that TB and CB isomerized into NB in the presence of $(C_2H_5)_3Al\text{-}TiCl_3$ catalyst and then polymerized to give a high-molecular-weight polymer of NB. The mechanism of the polymerization of butene-2 by the Ziegler-Natta catalyst will be described in detail in the next paper.

Summary

The effect of the methyl substituents of four butene isomers (IB, NB, TB and CB) on their polymerizations and copolymerizations has been investigated. None of these monomers homopolymerized in the presence of an ordinary radical or in that of anionic catalysts, but they were homopolymerized by cationic catalysts. The reactivity of these monomers toward their cationic polymerizations and radical copolymerizations has been found to decrease in the order of IB≫NB>TB—CB. These results have been interpreted on the basis of the steric effect and the chain transfer reactivity of the methyl substituents in these monomers.

These monomers, except for IB, can easily be homopolymerized by the Natta catalyst in the reactivity order of NB≫TB—CB. The resulting polymers from TB and CB have been confirmed to be the same as the polymer from NB, which consisted of the recurring unit of *n*-butene-1.

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[16] C. C. Price, *J. Polymer Sci.*, **1**, 83, (1946); **2**, 101 (1947); **3**, 772 (1948).

[17] C. Walling, E. R. Briggs, K. B. Wolfstirn and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 1537 (1948); C. Walling, D. Seymour and K. B. Wolfstirm, ibid., **70**, 1544 (1948).

[18] G. Natta, G. Dall'Asta, G. Mazzanti, I. Pasquon, A. Valvassori and A. Zambelli, ibid., **83**, 3343 (1961).