

CATIONIC POLYMERIZATION OF α , β -DISUBSTITUTED OLEFINS

A. MIZOTE, T. HIGASHIMURA, AND S. OKAMURA

Kyoto University, Kyoto, Japan

INTRODUCTION

It is well known that α , β -disubstituted olefins cannot usually be polymerized to high polymers, especially by free-radical-type polymerization. The difficulty of polymerization has been attributed to the steric repulsion induced by the β -substituted group in the transition state of the propagating reaction¹.

It can be presumed, however, that the introduction of an alkyl group at the β -position of the vinyl double bond increases the electron density of the carbon-carbon double bond and thus the olefins become more reactive, especially by cationic polymerization.

Experimental results, however, showed these monomers to have rather low reactivity. For instance, C. G. Overberger and his colleagues (1958)² concluded that the steric effect of the β -alkyl group in styrene derivatives was so large that these monomers could not be polymerized into high polymers even by the cationic mechanism, in spite of the electron-donating property of the β -alkyl substituent. Usually, the electronic effect of the β -substituted group combines with the steric effect in the monomer reactivity and separation has not been previously tried. We should like to discuss first the effect of the β -methyl group of β -methylstyrenes and propenyl ethers (β -methyl vinyl ethers) in the copolymerization technique.

It is also interesting to study the reactivities of *cis*- and *trans*-isomers in the polymerization of α , β -disubstituted olefins. In the free-radical polymerization of fumaric and maleic esters, as already reported by F. R. Mayo and his colleagues (1948)³, the *trans*-isomer was more reactive than the *cis*-isomer. This fact was explained by the large resonance stabilization of the propagating radical formed from the *trans*-isomer at the transition state of the propagating reaction.

In the cationic polymerization of α , β -disubstituted olefins a few experimental results have been reported. C. G. Overberger found that in the cationic polymerization of β -methylstyrenes the *trans*-isomer was a little more reactive than the *cis*-isomer. P. H. Plesch and his colleagues (1958)⁴ observed that the less stable *cis*-stilbene was more reactive than the *trans*-isomer in cationic polymerization. Recently, J. Furukawa and his coworkers⁵ studied the reactivity of α , β -unsaturated ether by hydrolysis and suggested that the *trans*-isomer was more stable than the *cis*-isomer. Many

different results have now been reported for the reactivity difference between *cis*- and *trans*-isomers.

We should like to discuss, secondly, the reactivity difference between isomers in the cationic polymerization of α,β -disubstituted olefins. It is also important to know the type of double bond opening for the investigation of the propagation reaction in ionic polymerization.

G. Natta and his colleagues⁶ have concluded from x-ray diffraction on the di-tactic structure of polymers that the double bond of *trans*-propenyl ether usually opened in *cis*-type in the cationic polymerization. From x-ray examination, however, it is very difficult to know the steric structure of a polymer, or to discuss quantitatively the type of opening of a double bond, especially when the polymer is amorphous.

Finally, we should like to discuss the type of opening of the monomer double bond in the cationic polymerization of α,β -disubstituted olefins by n.m.r. investigation.

All these three factors are very important, we believe, in discovering the general characteristics of ionic polymerization of vinyl monomers.

CHANGE OF REACTIVITIES BY INTRODUCTION OF β -METHYL GROUP

Here the effects of the β -methyl group of β -methylstyrenes and propenyl ethers (β -methyl vinyl ethers) are studied by comparison of the monomer reactivity ratios in copolymerization with the corresponding β -unsubstituted monomers.

Styrenes⁷

We chose monomer pairs for which the propagating cations would be quite similar to each other in structure. Here the copolymerizations are made between styrene derivatives and β -methylstyrene derivatives in which nuclear substituents are the same, as shown in *Figure 1*. As seen in this *Figure* the propagating cations of styrenes and β -methylstyrenes can be

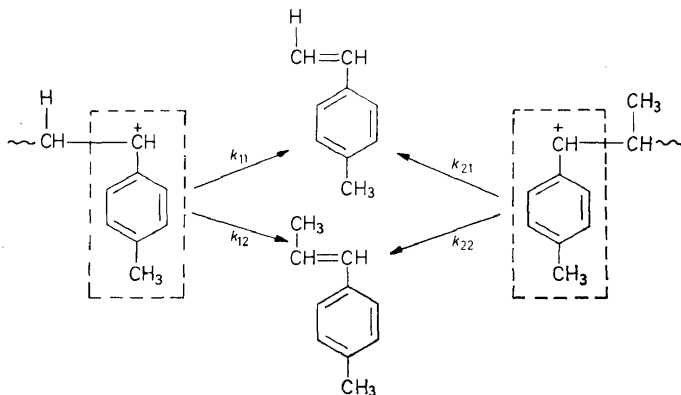

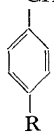


Figure 1. Copolymerization of styrenes with β -methylstyrenes

considered to be quite similar, because the inductive effect of the β -methyl group for the growing cation may be small for the charge stabilization.

The values of monomer reactivity ratios obtained here are summarized in Table 1. If the β -methyl group had no steric repulsion in the propagating

Table 1. Cationic copolymerization of styrenes (M_1) and β -methylstyrene (M_2)

M_1	M_2	R	r_1	r_2
$\text{CH}_2=\text{CH}$ 	CH_3 $ $ $\text{CH}=\text{CH}$ 	—H	1.8 ± 0.2	0.07 ± 0.02
		— CH_3	1.3 ± 0.3	0.04 ± 0.04
		— OCH_3	1.2 ± 0.2	0.04 ± 0.02

step, then $r_1 (=k_{11}/k_{12})$ should be equal to $1/r_2 (=k_{21}/k_{22})$. From the observed values, however, all r_2 -values are found to be much smaller than expected when $r_2 = 1/r_1$. The results in this table showing all $r_1 > 1$ and $1/r_2 > 1$, can be interpreted as indicating that the lowered reactivity of β -methylstyrenes is due to the steric effect of the β -methyl group.

Now we should like to make a quantitative examination of the lowering of reactivities of β -methylstyrenes. The influence of monomer structure on the free energy of the propagating reaction can be expressed as the sum of the polar, resonance and steric factors, given by Branch and Calvin⁸ as:

$$-\Delta F^\ddagger = P + R + S = RT \ln (k/k_0)$$

$$\log (k/k_0) = F_P + F_R + F_S$$

where F_P is the polar factor, F_R the resonance factor, and F_S the steric factor.

Applying this relation to copolymerization, we obtain

$$\log 1/r_1 = \log k_{12}/k_{11} = F_P + F_R + F_S$$

$$\log r_2 = \log k_{22}/k_{21} = F_P' + F_R' + F_S'$$

Here propagating cations, M_1^+ and M_2^+ might be the same, in resonance and polar factors, then,

$$F_R + F_P = F_R' + F_P'$$

$$\therefore \log r_2 - \log 1/r_1 = F_S' - F_S$$

$$F_S \ll F_S'$$

$$\therefore \log r_2 - \log 1/r_1 = F_S'$$

Then, the steric factor can be expressed by $(\log r_2 - \log 1/r_1)$ being between $-1.0 \sim -1.3$, calculated in this table. This means that the rate of homopolymerization is depressed by a factor of $1/10 \sim 1/20$ compared with the corresponding styrenes, due to the steric repulsion of the β -methyl group.

Vinyl ethers⁹

For the estimation of reactivity, propenyl ethers were copolymerized with vinyl ethers, in which monomer reactivity ratios were determined by measuring the amount of residual monomers by gas chromatography. As shown in Table 2, the monomer reactivity of propenyl *n*-butyl ether, here (M_1), was found to be surprisingly higher than that of vinyl ether, here (M_2).

Table 2. Monomer reactivity ratio in the copolymerization of propenyl ether ($\text{CH}_3\text{CH}=\text{CHOR}$), (M_2), with the corresponding vinyl ether ($\text{CH}_2=\text{CHOR}$), (M_1), by $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$ ($[M]_0$: 10 vol. %, $[C]$: 2 mmole/l., -74 to -78°C)

Solvent		Toluene ^a		Methylene chloride ^b	
Monomer	Geometric structure	r_1	r_2	r_1	r_2
Ethyl	<i>cis</i>	0.35 ± 0.1	4.0 ± 0.5	—	—
	<i>trans</i>	0.94 ± 0.1	0.94 ± 0.1	—	—
<i>n</i> -Butyl ³	<i>cis</i>	—	—	0.50 ± 0.2	4.0 ± 1.0
	<i>trans</i>	—	—	0.80 ± 0.3	2.3 ± 0.3
Isopropyl	<i>cis</i>	1.1 ± 0.2	0.80 ± 0.4	—	—
	<i>trans</i>	4.9 ± 0.4	0.19 ± 0.05	—	—
<i>tert</i> -Butyl	<i>cis</i>	2.2 ± 0.4	0.28 ± 0.08	—	—
Isobutyl ⁴	<i>cis</i>	—	—	0.29 ± 0.05	2.20 ± 0.14
	<i>trans</i>	—	—	1.04 ± 0.04	0.90 ± 0.03

^a Toluene contains 5 vol. % methylene chloride as an internal standard for the gas-chromatographic measurement.

^b Methylene chloride contains 5 vol. % of toluene for the same reason.

In both the *cis*- and *trans*-isomers, propenyl ethyl and *n*-butyl ethers have larger reactivities than corresponding vinyl ethers. In the copolymerization of β -methylstyrene with unsubstituted styrene, the steric hindrance makes the polymerization of β -methylstyrene difficult. This is in contradiction with the results for propenyl ether. However, propenyl ethers having a branched alkoxy group at the first carbon atom after ether oxygen (isopropyl and *t*-butyl propenyl ethers) were less reactive than the corresponding vinyl ethers.

β -Alkoxy styrenes¹⁰

It is interesting to study the behaviour of β -alkoxy styrenes in cationic polymerization. If the β -alkoxy styrenes act as the styrene type monomers,

the polymerizability should decrease with the increase of size of the β -alkoxy group due to the increase of steric hindrance. On the other hand, if the β -alkoxystyrenes act as the vinyl ether type monomers, the reactivity is expected to rise as the size of alkoxy group increases.

Here the monomers used are β -methoxy-, β -ethoxy-, β -*n*-propoxy- and β -*n*-butoxy-styrenes. From the copolymer composition curves of β -alkoxy-styrenes with vinyl ether, the monomer reactivity ratio is calculated. The order of reactivity found in these monomers is shown in *Table 3*. We can consider that β -alkoxystyrenes act as the vinyl-ether-type monomers.

Table 3. Monomer reactivity ratios of the copolymerization of vinyl-*n*-butyl ether (M_1) with β -alkoxystyrenes (M_2)

	β -Methoxy	β -Ethoxy	β - <i>n</i> -Propoxy	β - <i>n</i> -Butoxy
r_1	0.55	0.45	0.40	0.25
r_2	0.15	0.20	0.25	0.45

As reported previously, in the case of cationic polymerization of vinyl ethers, the molecular weight of the resultant polymer increases with the decreasing polarity of solvent but decreases in the case of styrene derivatives. In the homopolymerization of β -methoxystyrene catalysed by SnCl_4 , the high molecular weight polymer was obtained in a non-polar solvent such as toluene. A similar tendency is found in the polymerization of vinyl ethers.

These results suggest that the growing end of β -alkoxystyrene is a similar structure to that of vinyl ether. Now β -alkoxystyrene can be regarded as β -phenyl vinyl alkyl ether in the propagation reaction.

REACTIVITIES OF *cis*- AND *trans*-ISOMERS

In cationic polymerization the *trans*-isomer of β -methylstyrenes² was reported to be a little more reactive than the *cis*-isomer. However in the polymerization of stilbene, the *cis*-isomer was recognized to be more reactive than the *trans*-isomer⁴.

As already shown in *Table 2*, *cis*-propenyl ether is more reactive than the *trans*-isomer in the copolymerization with vinyl ether. We should next like to clarify the difference in reactivities of *cis*- and *trans*-isomers in α,β -disubstituted olefins.

Styrene derivatives¹¹

The residual monomer composition in the polymerization of the mixture of two isomers of β -methylstyrene and of β -methyl-*p*-methoxystyrene (i.e. anethol) is measured by gas chromatography. In this experiment, no isomerization could occur during polymerization. If the nature of the growing end is assumed to be the same in both *cis*- and *trans*-isomers, the gradients of first-order plots represent the polymerizability of both monomers. Polymerization was carried out in toluene or ethylene dichloride with stannic chloride or boron fluoride etherate at 0°C. It was found that the *trans*- β -methylstyrene was 1.3 ~ 1.5 times more reactive than the *cis*- β -methylstyrene against styrene-carbonium ion. The copolymerization between the

trans- and the *cis*-isomer of β -methylstyrene showed little difference in their monomer reactivities.

In contrast to β -methylstyrene, the *cis*-anethole was 1.5 ~ 2.0 times more reactive than the *trans*-anethole, estimated by the copolymerization between the *trans*- and the *cis*-isomer of anethole.

Propenyl ethers⁹

Propenyl ethers having various molar ratios of *cis*- and *trans*-isomers were polymerized in toluene with BF_3OEt_2 at -78°C , and the gradients of monomer consumption of first-order plots are compared as the polymerizabilities. As shown in Figure 2, *cis*-isomers have larger reactivities than those of *trans*-isomers.

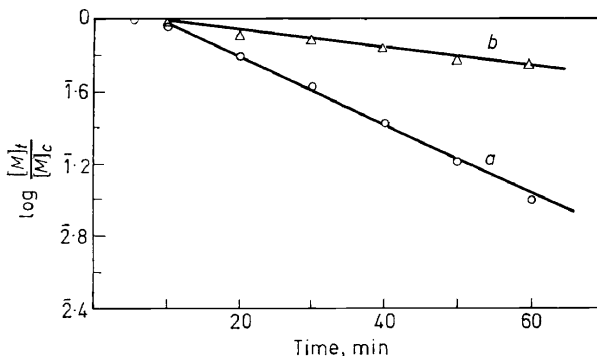


Figure 2. First-order plot for the monomer concentration in the copolymerization of *cis*- and *trans*-isopropyl propenyl ether.

a (○): *cis*-isopropyl propenyl ether

b (△): *trans*-isopropyl propenyl ether

$$\frac{d[M_c]}{d[M_i]} = \frac{k_{pc}[M_c]}{k_{pt}[M_i]}$$

Table 4. Relative reactivity of *cis*- and *trans*-propenyl ether by $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$. ($[M]_0$: 10 vol. %, $[C]$: 2-4 mmole/l., -74 to -78°C)

Monomer	Solvent	$(k_p)_{cis}/(k_p)_{trans}$
Methyl	Toluene ^a	3.7
	Methylene chloride ^b	---
Ethyl	Toluene	2.4
	Methylene chloride	1.4
Isopropyl	Toluene	3.7
	Methylene chloride	2.2
<i>n</i> -Butyl	Toluene	1.9
	Methylene chloride	1.5
Isobutyl	Ethyl benzene	6.4
	Methylene chloride	2.2

^a Toluene contains 5 vol. % of methylene chloride as an internal standard for the gas-chromatographic measurement.

^b Methylene chloride contains 5 vol. % of toluene for the same reason.

The copolymerization of the *cis*- and *trans*-isomers of propenyl *n*-butyl ether was examined and the monomer reactivity ratios of the *cis*-isomer, $r_c = 1.35 \pm 0.1$, and the *trans*-isomer, $r_t = 0.74 \pm 0.1$, were obtained. The *cis*-isomer has a larger reactivity ratio than the *trans*-isomer and these two values satisfy the relationship $r_1 r_2 = 1.0$. The nature of the growing end is therefore considered to be the same in both *cis*- and *trans*-isomers.

The reactivity ratios of the *cis*- and *trans*-isomers of propenyl ethers are summarized in Table 4. The *cis*-isomer is more reactive than the *trans*-isomer irrespective of the kind of monomer and the polarity of the solvent.

STEREOREGULATED POLYMERIZATION

G. Natta and his coworkers⁶ have already investigated the stereoregulated polymerization of propenyl alkyl ether and found that the *trans*-isomer was polymerized into crystalline threo-di-isotactic polymer, but the *cis*-isomer was polymerized into an amorphous polymer whose stereostructure was not revealed by x-ray examination.

We have studied the polymerization of propenyl ethers to crystalline polymers by homogeneous and heterogeneous catalysts.

Homogeneous and heterogeneous catalysts¹²

BF_3OEt_2 and AlEtCl_2 were used as homogeneous catalysts at -78°C , and the $\text{Al}_2(\text{SO}_4)_3/\text{H}_2\text{SO}_4$ complex catalyst was used as a heterogeneous catalyst at 0°C in *n*-hexane, toluene or methylene chloride as solvents. The experimental results are summarized in Tables 5 and 6.

Table 5. Stereospecific polymerization of $\text{CH}_3\cdot\text{CH}=\text{CHOR}$ by $\text{BF}_3\cdot\text{OEt}_2$ at -78°C . ($[M]_0$; 5 vol. %, $[C]$; 2-4 mmole/l, toluene)

Monomer	Cryst.	m.p. ($^\circ\text{C}$)
Methyl <i>cis</i>	×	150
<i>trans</i>	○	
Ethyl <i>cis</i>	×	207
<i>trans</i>	○	
Isopropyl <i>cis</i>	×	211
<i>trans</i>	○	
<i>n</i> -Butyl <i>cis</i>	×	ca. 100
<i>trans</i>	○	
<i>tert</i> -Butyl <i>cis</i>	○	>250

○: Crystalline, ×: Amorphous

By the homogeneous catalyst system the *trans*-isomer was polymerized into a crystalline polymer. By the heterogeneous catalyst, on the other hand, the *cis*-isomer was converted into crystalline polymer.

X-ray diffraction patterns of both crystalline polymers obtained by homogeneous and heterogeneous catalysts, are recognized to be completely different as shown in the example of poly(propenyl isopropyl ether) in

Table 7. As G. Natta⁶ has shown the *trans*-isomer produced threo-di-isotactic polymer, then the poly-*cis*-crystalline polymer obtained here might have erythro-di-isotactic structure.

On the other hand, the x-ray diffraction pattern and n.m.r. spectrum of poly(methyl propenyl ether) obtained from the *cis*-isomer by $\text{Al}_2(\text{SO}_4)_3/\text{H}_2\text{SO}_4$ complex are the same as that obtained from the *trans*-isomer by $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$. This means that threo-di-isotactic polymer is produced from *cis*-methyl propenyl ether.

As shown in Table 5, the only exception is the case of propenyl *t*-butyl ether in which the homogeneous system can produce crystalline polymer even in the *cis*-isomer. This is considered to be due to the steric hindrance induced both by β -methyl and bulky *t*-butoxy groups.

Table 6. Stereospecific polymerization of $\text{CH}_3 \cdot \text{CH}=\text{CHOR}$ by $\text{Al}_2(\text{SO}_4)_3/\text{H}_2\text{SO}_4$ complex at 0°C.
([M]₀; 20 vol. %, [C]; 0.4 g/100 ml, toluene)

Monomer		Cryst.	m.p. (°C)
Methyl	<i>cis</i>	○	230
	<i>trans</i>	—	
Ethyl	<i>cis</i>	○	191
	<i>trans</i>	—	
Isopropyl	<i>cis</i>	○	204
	<i>trans</i>	—	
<i>n</i> -Butyl	<i>cis</i>	○	ca. 100
	<i>trans</i>	oily	

○: Crystalline, —: No polymerization

Table 7. X-ray diffraction pattern of crystalline poly($\text{CH}_3\text{CH}=\text{CHOiPr}$)

<i>trans</i> ~ $\text{BF}_3 \cdot \text{OEt}_2$		<i>cis</i> ~ $\text{Al}_2(\text{SO}_4)_3/\text{H}_2\text{SO}_4$	
d (Å)	Strength	d (Å)	Strength
9.93	W		
8.78	VS	8.02	VS
6.33	S	6.00	M
5.06	M	5.38	W
4.29	S	4.68	W
3.69	W	4.17	S
2.83	W	2.89	W
2.20	W	2.23	W

Type of opening of double bond¹³

It is very important to know the type of double bond opening (i.e., *cis*- and *trans*-openings) for the investigation of the propagation reaction in the ionic polymerization. In the cationic polymerization of *trans*-propenyl ethers, G. Natta and his colleagues have concluded that the double bond of

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monomers opens in *cis*-type. However, in the x-ray examination adopted, quantitative evaluation of the steric structure is very difficult. When an amorphous polymer is obtained, the x-ray diffraction method is of little use.

In anionic polymerization, the double bond opening has been studied by the n.m.r. spectrum in the case of α,β -deuterium-2-acrylates by T. Yoshino (1964)¹⁴ and C. Schuerch and his coworkers (1964)¹⁵. Here the di-tacticity of poly(methyl propenyl ether) obtained by the cationic polymerization has been studied by n.m.r. spectra.

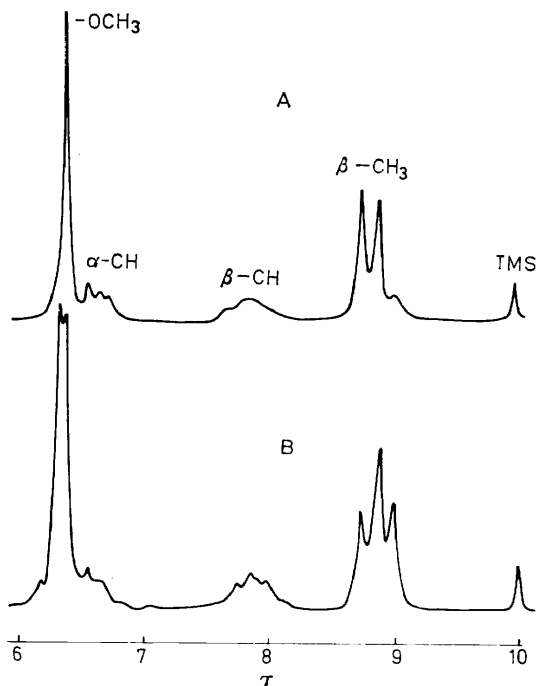


Figure 3. N.m.r. spectra of poly(methyl propenyl ethers) obtained by $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ in toluene at -78°C ($[M]_0$: 10 vol.%, $[C] = 3$ mmole/l.)

A *cis/trans* ratio in monomer mixture: 1/9

B *cis/trans* ratio in monomer mixture: 8/2

Two kinds of monomer mixture with different mole ratios of *cis*- and *trans*-isomers were used, that is, the *cis/trans* ratio equals to 1/9 and 8/2. N.m.r. spectra of polymer were measured in *o*-dichlorobenzene solution (10 w/v %) in a sealed tube at 160°C using the Varian HR-60 instrument. The n.m.r. spectra of β -methyl protons of the polymer were decoupled from β -methine proton by the side bond method, to know the amount of the di-tactic fraction in polymer. Figure 3 shows the n.m.r. spectra of polymers obtained by BF_3OEt_2 at -78°C . The spectrum of β -methyl protons of polymer obtained from *cis/trans* = 1/9 mixture is clearly different from that of 8/2. To study the di-tactic fractions of a polymer quantitatively, the n.m.r. spectra of β -methyl protons are decoupled from the β -methine proton. As shown in

Figure 4 the spectra of β -methyl protons consist of two signals at τ 8.78 and τ 8.89. The intensity of τ 8.78 is much stronger than that of τ 8.89, in the polymer obtained from *trans*-rich mixture. The intensity of the single at

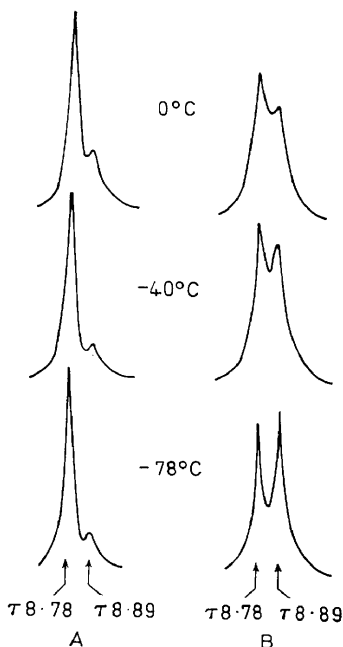


Figure 4. N.m.r spectra of β -methyl protons decoupled from β -methine proton in poly(methyl propenyl ethers) obtained by $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ in toluene at various polymerization temperatures. ($[M]_0$: 10 vol.%, $[C] = 3$ mmole/l)

A *cis/trans* ratio in monomer mixture: 1/9

B *cis/trans* ratio in monomer mixture: 8/2

τ 8.89 for the polymer obtained from *cis*-rich monomer mixture increases with lowering polymerization temperature.

G. Natta has shown that *trans*-alkenyl ethers produce the threo-di-isotactic polymer, therefore, poly(*trans*-methyl propenyl ether) obtained by BF_3OEt_2 at a low temperature should be the threo-di-isotactic structure. From these results, the signals of β -methyl protons at τ 8.78 and τ 8.89 are assigned as spectra based on threo- and erythro-di-isotactic diads, respectively.

On the basis of the assignment of β -methyl protons, the content of the threo- and erythro-di-isotactic diads can be determined quantitatively. These results are shown in Table 8 together with the polymerization conditions and properties of the polymers.

The polymers obtained from a *trans*-rich mixture are highly crystalline and contain more than 80 per cent of the threo-di-isotactic diad. On the other hand, the polymer obtained from a *cis*-rich mixture is amorphous and contains a mixture of the threo- and erythro-di-isotactic diads.

On the basis of polymer structure and composition, the type of double-bond opening may be discussed quantitatively. If the probability of *trans*-

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 Table 8. Polymerization conditions and properties of poly(methyl propenyl ether)
 ($[M]_0 = 10$ vol.%, $[BF_3OEt_2] = 3$ mmole/l., $t = 2$ h, solvent: toluene)

cis/trans in Monomer mole ratio	Polymeri- zation temp. °C	Conversion %	$[\eta]$ 100ml/g	Crystal- linity	Threo-di isotactic fraction %	Erythro-di- isotactic fraction %
1/9	-40	55	0.10	cryst.	82.6	17.4
1/9	-78	32	0.30	cryst.	85.7	14.3
8/2	-40	68	0.09	amorph.	51.9	48.0
8/2	-78	66	0.27	amorph.	44.4	55.6

opening in *cis*-monomer is defined as A (then, the probability of *cis*-opening is $1 - A$) and the probability of *trans*-opening in *trans*-monomer is defined as B (then, the probability of *cis*-opening is $1 - B$), we can obtain:

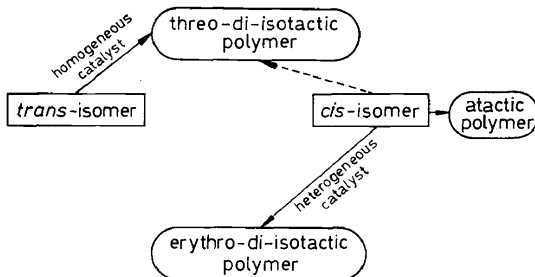
$$\frac{d[M_c]}{d[M]} A + \frac{d[M_t]}{d[M]} (1 - B) = (\text{Threo-di-isotactic fraction})$$

where $d[M_c]$, $d[M_t]$ and $d[M]$ are the mole concentrations of *cis*-, *trans*- and total monomer in the polymer, respectively. At a constant temperature, the type of opening is considered to be constant in different compositions and the chain end formed does not rotate freely. Therefore A and B can be calculated from the experimental results. The percentages of *cis*- and *trans*-openings thus obtained are summarized in Table 9.

From these results, it is concluded that the double bond in a *trans*-monomer is opened exclusively in the *cis*-type while in a *cis*-monomer, *cis*- and *trans*-opening takes place at almost the same rates in a homogeneous catalyst system.

Table 9. Fraction of double bond opening at various polymerization temperatures

Polymerization temperature °C	cis-Isomer		trans-Isomer	
	cis-Opening %	trans-Opening %	cis-Opening %	trans-Opening %
0	47	53	80	20
-40	50	50	89	11
-78	60	40	ca. 100	ca. 0



Stereospecific polymerization of *cis*- and *trans*-isomers in propenyl ethers

As a preliminary conclusion, we would like to emphasize the following six points.

First, by quantitative examination of the lowering of reactivities of β -methylstyrenes, the effect of steric repulsion of the β -methyl group is $1/10$ – $1/20$, compared to the styrenes.

Second, in the case of propenyl *n*-alkyl ethers, the reactivities of β -methyl-substituted monomers have been found to be larger than that of unsubstituted monomer by electronic effect. However, in branched-alkyl ether, the relationship was similar in styrene derivatives for which the steric effect as well as electronic effect must be considered both in α - and β -positions.

Third, from the reactivity behaviour, β -alkoxystyrenes are considered to be β -phenyl alkyl vinyl ethers.

Fourth, a *cis*-isomer has a larger reactivity than a *trans*-isomer, and, again styrene derivatives and branched alkyl vinyl ethers both have the tendency for reactivity to be larger in *trans*- than in *cis*-isomers, or the differences become smaller.

Fifth, not only *trans*-isomers but also *cis*-isomers could be polymerized into crystalline polymers, using homogeneous and heterogeneous catalysts, respectively. Thus, crystalline analysis by the x-ray diffraction method is made possible.

Sixth, by n.m.r. spectra of β -methyl protons, the type of opening was quantitatively measured. In the case of amorphous polymers, the proportion of *cis*- to *trans*-opening is approximately 50 : 50.

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