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Microstructure of Poly(methyl propenyl ether)

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ABSTRACT: The chain statistics for ditactic polymer is developed to the reversible double Markovian process. The NMR spectra of poly(methyl propenyl ether) cationically obtained with $BF_3 \cdot O(C_2H_5)_2$ and sulfuric acid—aluminum sulfate complex are analyzed according to these statistics, and the lack of *erythro-meso* structure is deduced in the polymer obtained with the former catalyst. Finally, two kinds of possible polymerization mechanisms are proposed for the cationic polymerization of *cis*-methyl propenyl ether with $BF_3 \cdot O(C_2H_5)_2$. One is that adding monomers open always in *trans* form but the attacks on monomers are random. The other is that adding monomers open randomly but the attacks on monomers cause the *meso* form.

KEY WORDS Microstructure / NMR / Double Markovian / Reversible Markovian / Poly(methyl propenyl ether) / Boron Trifluoride / Sulfuric Acid—Aluminum Sulfate Complex /

In order to investigate the polymerization mechanism of α-olefins there are two important problems, namely (1) the regularity in opening of the double bond in monomers and (2) that in attack on adding monomers in the sense of stereospecificity. These problems cannot be detected for α-olefins themselves because of the equivalence of two substituents to the β carbon. However, the study of α, β-disubstituted olefins through the microstructures of the polymers serves to guide us on the problem, because the microstructures are decided by the two kinds of regularities above mentioned.

Since Natta and his colleagues[1] have already examined deuterated polypropylene in this manner, many authors have studied the polymerization mechanism of α, β-disubstituted olefins, in which deuterated α-olefins are included, with the aid of X-ray diffraction, high resolution nuclear magnetic resonance (NMR) and other analyses for the polymers obtained. On the other hand, Frisch and his colleagues[2] have considered the reversibility of the model when the ditacticity of the polymers from α, β-disubstituted olefins is analyzed by Markovian statistics. The irreversibility appears only in higher order Markovian statistics greater than the third one. The NMR spectra of the polymers obtained from α, β-disubstituted olefins have been analyzed without the consideration of such an irreversibility, because the peaks in the spectra considerably coalesce with each other.

The first section of this paper is devoted to the representation of the transition probabilities in ditactic polymers on the basis of reversible Markovian statistics derived by Frisch and his colleagues.

The second section deals with the analysis of the NMR spectra of poly(methyl propenyl ether) as an example of ditactic polymer. The spectra are analyzed by the representation obtained in the first section.

The last section deals with the consideration of the cationic polymerization mechanism in methyl propenyl ether.

REPRESENTATION OF THE TRANSITION PROBABILITIES IN DITACTIC POLYMERS

Ditacticity is considered in a similar fashion to the tacticity of vinyl polymers, *i.e.*, it is described by the terms of monoad, dyad, triad, and so on. But, it is convenient to define the term "dyad" for the microstructure decided by the

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configurations between the substituents of two adjacent skeletal carbons and not of three. Generally, the term "*n*-ad" is defined for that of *n* adjacent skeletal carbons and not of $2n-1$. Care must therefore be taken to distinguish between the definition of *n*-ad from that for other α-olefins.

Two substituents bonded with α and β carbons are denoted as R_1 and R_2, respectively. The terms, "*meso*" and "*racemic*" are defined as the configurations in which adjacent R_1 and R_2 groups are located in the same and the opposite side, respectively, to the plane constituted by skeletal bonds when the polymer has *trans*-zigzag conformation. If the sense of the propagation in a growing chain is considered, there are four kinds of dyad as shown in Table I. In this table the small letters m and r are *meso* and *racemic* dyads, respectively of $[R_2, R_1]$ type, and the capital letters M and R are those of $[R_1, R_2]$ type. Possible sequences in triads, tetrads and pentads are also shown in this table. Every structure corresponding to every dyad or triad is described with Fischer projection in this table.

Some kinds of reduction relation hold between the occurrence frequencies of *n*-ads for a sufficiently long chain. Such relations are listed in Table II up to pentads. In this table the first equation for every *n*-ad shows the normalization condition. All other equations are derived from the requirement of the continuity of the chain. For example, [m]+[r] is equal to the normalized frequency of the dyad constituted by $[R_2, R_1]$, while [M]+[R] is that by $[R_1, R_2]$; the equality between these two quantities leads to the second equation for the dyad.

If we want to observe such *n*-ad structures of polymers, we are limited to the observation of dead polymers, not of growing ones. This matter necessarily leads to the ignorance between an *n*-ad and its reverse, for example [m] ($-\underset{R_2}{\mathrm{C}}-\overset{R_1}{\mathrm{C}}-$) and [M] ($-\underset{R_1}{\mathrm{C}}-\overset{R_2}{\mathrm{C}}-$), and so on. Then, if observable *n*-ads are denoted by the quantities enclosed by parentheses, we have the relations between their normalized frequencies and the quantities described in Table I as follows

$$
\begin{aligned}
&(\mathrm{m})=[\mathrm{m}]+[\mathrm{M}]\\
&(\mathrm{mR})=[\mathrm{mR}]+[\mathrm{rM}] \qquad (1)\\
&(\mathrm{mMm})=[\mathrm{mMm}]+[\mathrm{MmM}]
\end{aligned}
$$

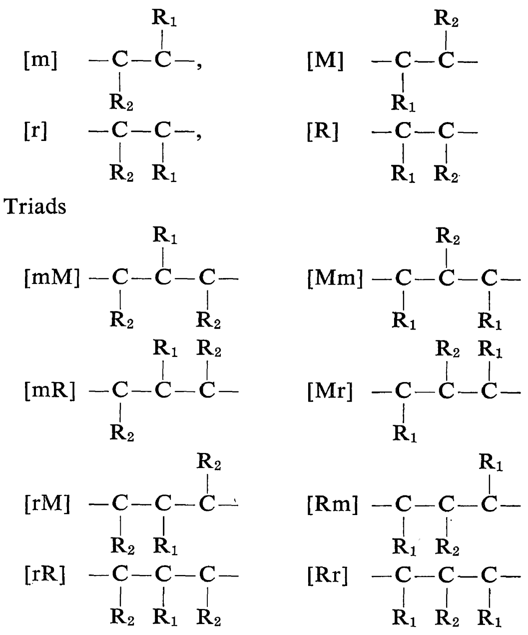
and so on.

When the propagation mechanism in ditactic polymer is described and analyzed by the stochastic process, the information obtained is somewhat ambiguous due to the above-mentioned

Table I. Possible *n*-ads and their structures in ditactic polymers

Dyads

meso m, M, *racemic* r, R,



[m] $-\underset{R_2}{\mathrm{C}}-\overset{R_1}{\mathrm{C}}-$, [M] $-\underset{R_1}{\mathrm{C}}-\overset{R_2}{\mathrm{C}}-$

[r] $-\underset{R_2}{\mathrm{C}}-\underset{R_1}{\mathrm{C}}-$, [R] $-\underset{R_1}{\mathrm{C}}-\underset{R_2}{\mathrm{C}}-$

Triads

[mM] $-\underset{R_2}{\mathrm{C}}-\overset{R_1}{\mathrm{C}}-\underset{R_2}{\mathrm{C}}-$ [Mm] $-\underset{R_1}{\mathrm{C}}-\overset{R_2}{\mathrm{C}}-\underset{R_1}{\mathrm{C}}-$

[mR] $-\underset{R_2}{\mathrm{C}}-\overset{R_1}{\mathrm{C}}-\overset{R_2}{\mathrm{C}}-$ [Mr] $-\underset{R_1}{\mathrm{C}}-\overset{R_2}{\mathrm{C}}-\overset{R_1}{\mathrm{C}}-$

[rM] $-\underset{R_2}{\mathrm{C}}-\underset{R_1}{\mathrm{C}}-\overset{R_2}{\mathrm{C}}-$ [Rm] $-\underset{R_1}{\mathrm{C}}-\underset{R_2}{\mathrm{C}}-\overset{R_1}{\mathrm{C}}-$

[rR] $-\underset{R_2}{\mathrm{C}}-\underset{R_1}{\mathrm{C}}-\underset{R_2}{\mathrm{C}}-$ [Rr] $-\underset{R_1}{\mathrm{C}}-\underset{R_2}{\mathrm{C}}-\underset{R_1}{\mathrm{C}}-$

Tetrads

[mMm],	[mMr],	[mRm],	[mRr],
[rMm],	[rMr],	[rRm],	[rRr],
[MmM],	[MmR],	[MrM],	[MrR],
[RmM],	[RmR],	[RrM],	[RrR],

Pentads

[mMmM],	[mMmR],	[mMrM],	[mMrR],
[mRmM],	[mRmR],	[mRrM],	[mRrR],
[rMmM],	[rMmR],	[rMrM],	[rMrR],
[rRmM],	[rRmR],	[rRrM],	[rRrR],
[MmMm],	[MmMr],	[MmRm],	[MmRr],
[MrMm],	[MrMr],	[MrRm],	[MrRr],
[RmMm],	[RmMr],	[RmRm],	[RmRr],
[RrMm],	[RrMr],	[RrRm],	[RrRr].

Table II. Relations held between every *n*-ad in ditactic polymers

Dyads	$[m]+[M]+[r]+[R]=1$
	$[m]-[M]=[R]-[r]$
Triads	sum $=1$
	$[mM]-[Mm]=[Rm]-[mR]=[rR]-[Rr]=[Mr]-[rM]$
Tetrrds	sum $=1$
	$[mMm]-[MmM]=[RmM]-[mMr]=[MmR]-[rMm]$
	$[mRm]-[RmR]=[MmR]-[mRr]=[RmM]-[rRm]$
	$[rRr]-[RrR]=[MrR]-[rRm]=[RrM]-[mRr]$
	$[rMr]-[MrM]=[RrM]-[rMm]=[MrR]-[mMr]$
Pentads	sum $=1$
	$[mMmM]-[MmMm]=[RmMm]-[mMmR]=[MmMr]-[rMmM]$
	$[mRmR]-[RmRm]=[MmRm]-[mRmM]=[RmRr]-[rRmR]$
	$[rMrM]-[MrMr]=[MrMm]-[mMrM]=[RrMr]-[rMrR]$
	$[rRrR]-[RrRr]=[MrRr]-[rRrM]=[RrRm]-[mRrR]$
	$[mMrM]+[mMrR]=[MmMr]+[RmMr]$
	$[mMmR]+[rMmR]=[MmRm]+[MmRr]$
	$[rMmM]+[rMmR]=[MrMm]+[RrMm]$
	$[mRmM]+[rRmM]=[RmMm]+[RmMr]$
	$[mMrR]+[rMrR]=[MrRm]+[MrRr]$
	$[mRrM]+[mRrR]=[MmRr]+[RmRr]$
	$[rRmM]+[rRmR]=[MrRm]+[RrRm]$
	$[mRrM]+[rRrM]=[RrMm]+[RrMr]$

ignorance between the two kinds of *n*-ad, because we cannot estimate the value of the molar ratio between them. Therefore, we will treat the simplest case, *i.e.*, that this ratio is equal to unity, which means that an *n*-ad appears equally probable to its reverse one in a chain. Such a case is called a *reversible* stochastic process.[2]

In the first place the propagation mechanism will be described by the stochastic process with a simple Markovian. A simple Markovian process is completely described by the four kinds of conditional probabilities as follows.

$$\begin{array}{ll} P_{\mathrm{mM}}=a & P_{\mathrm{mR}}=1-a=\bar{a} \\ P_{\mathrm{rM}}=b & P_{\mathrm{rR}}=1-b=\bar{b} \\ P_{\mathrm{Mm}}=c & P_{\mathrm{Mr}}=1-c=\bar{c} \\ P_{\mathrm{Rm}}=d & P_{\mathrm{Rr}}=1-d=\bar{d} \end{array} \tag{2}$$

Dyads [m] and [M] are expressed with these conditional probabilities as follows.

$$\begin{array}{l} [\mathrm{m}]=[\mathrm{M}]P_{\mathrm{Mm}}+[\mathrm{R}]P_{\mathrm{Rm}} \\ [\mathrm{M}]=[\mathrm{m}]P_{\mathrm{mM}}+[\mathrm{r}]P_{\mathrm{mR}} \\ [\mathrm{m}]+[\mathrm{r}]=[\mathrm{M}]+[\mathrm{R}]=1/2 \end{array} \tag{3}$$

On the other hand, the reversible condition is introduced by

$$[\mathrm{m}]=[\mathrm{M}] \tag{4}$$

because the relation

$$[\mathrm{mR}]=[\mathrm{rM}] \tag{5}$$

is reduced to eq 4 with the aids of

$$\begin{array}{l} [\mathrm{m}]=[\mathrm{mM}]+[\mathrm{mR}] \\ [\mathrm{M}]=[\mathrm{mM}]+[\mathrm{rM}] \end{array} \tag{6}$$

Then, eq 2—6 lead to the relations for observable dyads as follows

$$\begin{array}{l} (\mathrm{m})=(b+d)/S \\ (\mathrm{r})=(\bar{a}+\bar{c})/S \end{array} \tag{7}$$

where

$$S=\bar{a}+b+\bar{c}+d \tag{8}$$

Similar relations can be obtained for observable *n*-ads. They are listed in Table III up to pentads.

If the propagation mechanism is described by the stochastic process up to double Markovian, we must introduce eight conditional probabilities instead of those in eq 2. They are as follows

$$\begin{array}{ll} P_{\mathrm{MmM}}=a & P_{\mathrm{MmR}}=1-a=\bar{a} \\ P_{\mathrm{MrM}}=b & P_{\mathrm{MrR}}=1-b=\bar{b} \\ P_{\mathrm{RmM}}=c & P_{\mathrm{RmR}}=1-c=\bar{c} \end{array}$$

$$\begin{array}{ll} P_{\mathrm{RrM}}=d & P_{\mathrm{RrM}}=1-d=\bar{d} \\ P_{\mathrm{mMm}}=e & P_{\mathrm{mMr}}=1-e=\bar{e} \\ P_{\mathrm{mRm}}=f & P_{\mathrm{mRr}}=1-f=\bar{f} \\ P_{\mathrm{rMm}}=g & P_{\mathrm{rMr}}=1-g=\bar{g} \\ P_{\mathrm{rRm}}=h & P_{\mathrm{rRr}}=1-h=\bar{h} \end{array} \tag{9}$$

Reversible conditions for this process are described by eight ($=2^3$) sets of equations

$$[\mathrm{xYz}]=[\mathrm{ZyX}] \tag{10}$$

where x, y, and z denote either m or r, and X, Y, and Z denote M or R corresponding to *x*, *y*, and *z*. There are some relations between the intensities of tetrads as shown in Table II.

Table III. Observable *n*-ads described by reversible Markovian process

Dyads

$(\mathrm{m})=(b+d)/S$

$(\mathrm{r})=(\bar{a}+\bar{c})/S$

Triads

$(\mathrm{mM})=a(b+d)/2S$

$(\mathrm{mR})=\bar{a}(b+d)/S$

$(\mathrm{rR})=\bar{b}(\bar{a}+\bar{c})/2S$

$(\mathrm{Mm})=c(b+d)/2S$

$(\mathrm{Mr})=d(\bar{a}+\bar{c})/S$

$(\mathrm{Rr})=\bar{d}(\bar{a}+\bar{c})/2S$

Tetrads

$(\mathrm{mMm})=ac(b+d)/S=4(\mathrm{mM})(\mathrm{Mm})/(\mathrm{m})$

$(\mathrm{mMr})=a\bar{c}(b+d)/S=2(\mathrm{mM})(\mathrm{Mr})/(\mathrm{m})$

$(\mathrm{mRm})=\bar{a}d(b+d)/S=(\mathrm{mR})(\mathrm{Mr})/(\mathrm{r})$

$(\mathrm{mRr})=\overline{ad}(b+d)/S=2(\mathrm{mR})(\mathrm{Rr})/(\mathrm{r})$

$(\mathrm{rMm})=bc(\bar{a}+\bar{c})/S=2(\mathrm{mR})(\mathrm{Mm})/(\mathrm{m})$

$(\mathrm{rMr})=b\bar{c}(\bar{a}+\bar{c})/S=(\mathrm{mR})(\mathrm{Mr})/(\mathrm{m})$

$(\mathrm{rRm})=\bar{b}d(\bar{a}+\bar{c})/S=2(\mathrm{rR})(\mathrm{Mr})/(\mathrm{r})$

$(\mathrm{rRr})=\overline{bd}(\bar{a}+\bar{c})/S=4(\mathrm{rR})(\mathrm{Rr})/(\mathrm{r})$

Pentads

$(\mathrm{mMmM})=a^2c(b+d)/2S=4(\mathrm{mM})^2(\mathrm{Mm})/(\mathrm{m})^2$

$(\mathrm{mMmR})=a\bar{a}c(b+d)/S=4(\mathrm{mM})(\mathrm{Mm})(\mathrm{mR})/(\mathrm{m})^2$

$(\mathrm{mMrM})=ab\bar{c}(b+d)/S=2(\mathrm{mM})(\mathrm{Mr})(\mathrm{mR})/(\mathrm{m})(\mathrm{r})$

$(\mathrm{mMrR})=a\overline{bc}(b+d)/S=4(\mathrm{mM})(\mathrm{Mr})(\mathrm{rR})/(\mathrm{m})(\mathrm{r})$

$(\mathrm{mRmR})=\bar{a}b\bar{c}(b+d)/S=(\mathrm{mR})^2(\mathrm{Mr})/(\mathrm{m})(\mathrm{r})$

$(\mathrm{mRrM})=b^2\bar{d}(\bar{a}+\bar{c})/2S=(\mathrm{mR})^2(\mathrm{Rr})/(\mathrm{r})^2$

$(\mathrm{mRrR})=\overline{bb}d(\bar{a}+\bar{c})/S=4(\mathrm{mR})(\mathrm{Rr})(\mathrm{rR})/(\mathrm{r})^2$

$(\mathrm{rMmR})=\bar{a}bc(\bar{a}+\bar{c})/2S=(\mathrm{mR})^2(\mathrm{Mm})/(\mathrm{m})^2$

$(\mathrm{rMrR})=\overline{ab}d(\bar{a}+\bar{c})/S=2(\mathrm{mR})(\mathrm{Mr})(\mathrm{rR})/(\mathrm{m})(\mathrm{r})$

$(\mathrm{rRrR})=\bar{b}\bar{d}(\bar{a}+\bar{c})/2S=4(\mathrm{rR})^2(\mathrm{Rr})/(\mathrm{r})^2$

$S=\bar{a}+b+\bar{c}+d$

These relations reduce the number of sets of independent equations to three as follows

$$\begin{aligned} [\mathrm{mMm}]&=[\mathrm{MmM}] \\ [\mathrm{rRr}]&=[\mathrm{RrR}] \\ [\mathrm{mRm}]&=[\mathrm{MrM}] \end{aligned} \tag{11}$$

Furthermore, the last equation in eq 11 can be reduced to

$$[\mathrm{mR}]=[\mathrm{rM}] \tag{11$'$}$$

with the aids of

$$\begin{aligned} [\mathrm{mR}]&=[\mathrm{mRm}]+[\mathrm{mRr}] \\ [\mathrm{rM}]&=[\mathrm{MrM}]+[\mathrm{RrM}] \end{aligned} \tag{12}$$

Intensities of triads are described with the aid of transition probabilities as follows

Table IV. Observable *n*-ads described by reversible double Markovian process

Triads

$(\mathrm{mM})=a(b-f)(d-h)/2S$

$(\mathrm{mR})=b(e-a)(d-h)/S$

$(\mathrm{rR})=\bar{d}(b-f)(e-a)/2S$

$(\mathrm{Mm})=e(b-f)(d-h)/2S$

$(\mathrm{Mr})=f(e-a)(d-h)/S$

$(\mathrm{Rr})=\bar{h}(b-f)(e-a)/2S$

Tetrads

$(\mathrm{mMm})=ae(b-f)(d-h)/S$

$(\mathrm{mMr})=cf(e-a)(d-h)/S$

$(\mathrm{mRm})=bf(e-a)(d-h)/S$

$(\mathrm{mRr})=d\bar{h}(b-f)(e-a)/S$

$(\mathrm{rMm})=\bar{a}e(b-f)(d-h)/S$

$(\mathrm{rMr})=\bar{c}f(e-a)(d-h)/S$

$(\mathrm{rMR})=\bar{b}f(e-a)(d-h)/S$

$(\mathrm{rRr})=\overline{dh}(b-f)(e-a)/S$

Pentads

$(\mathrm{mMmM})=a^2e(b-f)(d-h)/2S-(\mathrm{mMm})^2/4(\mathrm{Mm})$

$(\mathrm{mMmR})=\bar{a}ae(b-f)(d-h)/S=(\mathrm{mMm})(\mathrm{rMm})/2(\mathrm{Mm})$

$(\mathrm{mMrM})=bcf(e-a)(d-h)/S=(\mathrm{mMr})(\mathrm{mRm})/(\mathrm{Mr})$

$(\mathrm{mMrR})=\bar{b}cf(e-a)(d-h)/S=(\mathrm{mMr})(\mathrm{rRm})/(\mathrm{Mr})$

$(\mathrm{mRmR})=\bar{b}cf(e-a)(d-h)/S=(\mathrm{mRm})(\mathrm{rMr})/(\mathrm{Mr})$

$(\mathrm{mRrM})=d^2\bar{h}(b-f)(e-a)/2S=(\mathrm{mRr})^2/4(\mathrm{Rr})$

$(\mathrm{mRrR})=d\overline{dh}(b-f)(e-a)/S=(\mathrm{mRr})(\mathrm{rRr})/2(\mathrm{Rr})$

$(\mathrm{rMmR})=\bar{a}^2e(b-f)(d-h)/2S=(\mathrm{rMm})^2/4(\mathrm{Mm})$

$(\mathrm{rMrR})=\overline{bc}f(e-a)(d-h)/S=(\mathrm{rMr})(\mathrm{rRm})/(\mathrm{Mr})$

$(\mathrm{rRrR})=\bar{d}^2\bar{h}(b-f)(e-a)/2S=(\mathrm{rRr})^2/4(\mathrm{Rr})$

$S=\frac{1}{2}(a+e)(b-f)(d-h)+(b+f)(e-a)(d-h)$

$\quad\frac{1}{2}(\bar{d}+\bar{h})(e-a)(b-f)$

$$\begin{aligned}[\mathrm{aB}]&=[\mathrm{Ma}]P_{\mathrm{MaB}}+[\mathrm{Ra}]P_{\mathrm{RaB}}\\ [\mathrm{Ab}]&=[\mathrm{mA}]P_{\mathrm{MAb}}+[\mathrm{rA}]P_{\mathrm{rAb}}\end{aligned}\tag{13}$$

The solution of these equations leads to

$$\begin{gathered}\frac{a\bar{e}+\overline{ag}}{df+\bar{d}h}=\frac{\bar{a}g-c\bar{e}}{d\bar{f}-\bar{b}h}\\ ag/\overline{ag}=ce/\overline{ce}\\ bh/\overline{bh}=df/\overline{df}\end{gathered}\tag{14}$$

These relations are the necessary and sufficient conditions for the reversible double Markovian process.

On the basis of the fact there are usually only two kinds of steric structure observed for the β carbons in cationically polymerized ditactic

Table V. Relative intensities of *n*-ads for specialized Markovian processes

	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6
Dyads						
(m)	d/s	$(1+d)/s$	$1/s$	h/s	$(e-af)/s$	$(c+\bar{a})/s$
(r)	$\bar{c}/s$	$(\bar{a}+\bar{c})/s$	$\bar{a}/s$	$\bar{e}/s$	$(e-a)/s$	$\bar{a}/s$
Triads						
(mM)	$d/2s$	$a(1+d)/2s$	$a/2s$	$h/2s$	$a\bar{f}/2s$	$c/2s$
(mR)	0	$\bar{a}(1+d)/s$	$\bar{a}/2s$	0	$(e-a)/s$	$\bar{a}/s$
(rR)	$\bar{c}/2s$	0	0	$\bar{e}/2s$	0	0
(Mm)	$cd/2s$	$c(1+d)/2s$	$a/2s$	$eh/2s$	$e\bar{f}/2s$	$c/2s$
(Mr)	$\bar{c}d/s$	$d(\bar{a}+\bar{c})/s$	$\bar{a}/s$	$\bar{e}h/s$	$f(e-a)/s$	$\bar{a}/s$
(Rr)	$\overline{cd}/2s$	$\bar{d}(\bar{a}+\bar{c})/2s$	0	$\overline{eh}/2s$	$\bar{f}(e-a)/2s$	0
Tetrads						
(mMm)	cd/s	$ac(1+d)/s$	a^2/s	eh/s	$ae\bar{f}/s$	ac/s
(mMr)	$\bar{c}d/s$	$a\bar{c}(1+d)/s$	$a\bar{a}/s$	$\bar{e}h/s$	$cf(e-a)/s$	$\bar{a}c/s$
(mRm)	0	$\bar{a}d(1+d)/s$	$\bar{a}/s$	0	$f(e-a)/s$	$\bar{a}/s$
(mRr)	0	$\overline{ad}(1+d)/s$	0	0	$\bar{f}(e-a)/s$	0
(rMm)	0	$c(\bar{a}+\bar{c})/s$	$a\bar{a}/s$	0	$\bar{a}e\bar{f}/s$	$\bar{a}c/s$
(rMr)	0	$\bar{c}(\bar{a}+\bar{c})/s$	$\bar{a}^2/s$	0	$\bar{c}f(e-a)/s$	$\overline{ac}/s$
(rRm)	$\bar{c}d/s$	0	0	$\bar{e}h/s$	0	0
(rRr)	$\overline{cd}/s$	0	0	$\overline{eh}/s$	0	0
Pentads						
(mMmM)	$cd/2s$	$a^2c(1+d)/2s$	$a^3/2s$	$eh/2s$	$a^2ef/2s$	$a^2c/2s$
(mMmR)	0	$a\bar{a}c(1+d)/s$	$a^2\bar{a}/s$	0	$a\bar{a}e\bar{f}/s$	$a\bar{a}c/s$
(mMrM)	0	$a\bar{c}(1+d)/s$	$a\bar{a}/s$	0	$cf(e-a)/s$	$\bar{a}c/s$
(mMrR)	$\bar{c}d/s$	0	0	$\bar{e}h/s$	0	0
(mRmR)	0	$\overline{ac}(1+d)/s$	$\bar{a}^2/s$	0	$\bar{c}f(e-a)/s$	$\overline{ac}/s$
(mRrM)	0	$\bar{d}(\bar{a}+\bar{c})/2s$	0	0	$\bar{f}(e-a)/2s$	0
(mRrR)	0	0	0	0	0	0
(rMmR)	0	$\bar{a}c(\bar{a}+\bar{c})/2s$	$a\bar{a}^2/2s$	0	$\bar{a}^2e\bar{f}/2s$	$\bar{a}^2c/2s$
(rMrR)	0	0	0	0	0	0
(rRrR)	$\overline{cd}/2s$	0	0	$\overline{eh}/2s$	0	0

Case 1: $s=\bar{c}+d$
2: $s=1+\bar{a}+\bar{c}+d$
3: $s=1+\bar{a}$
4: $s=\bar{e}+h$
5: $s=2e-a-af$
6: $s=2\bar{a}+c$

polymers, the Markovian process is somewhat specialized as follows, namely, the effect of the absence of any triad structure on the process will be discussed.

Case 1. (mR)=0 in the reversible simple Markovian process: The conditions satisfying this requirement, $P_{rM}=P_{mR}=0$ lead to the reversible condition $P_{mR}\cdot P_{Rm}=P_{rM}\cdot P_{Mr}$, *i.e.*, this process is always reversible.

Case 2. (rR)=0 in the reversible simple Markovian process: From the conditions $P_{rR}=\bar{b}=0$, we have $\bar{c}=\bar{a}d$ as the reversible condition.

Case 3. (rR)=(Rr)=0 in the reversible simple Markovian process: From the conditions $P_{rR}=\bar{b}=P_{Rr}=\bar{d}=0$, we have $\bar{a}=\bar{c}$ as the reversible condition.

Case 4. (mR)=0 in the reversible double Markovian process: From the conditions $P_{MmR}=P_{RmR}=P_{MrM}=P_{RrM}=0$, reversible conditions eq 14, are always satisfied.

Case 5. (rR)=0 in the reversible double Markovian process: Reversible conditions can be obtained by the substitution of $P_{MrR}=\bar{b}=P_{RrR}=\bar{d}=0$ into eq 14.

Case 6. (rR)=(Rr)=0 in the reversible double Markovian process: From the conditions $P_{MrR}=P_{RrR}=P_{mRr}=P_{MRr}=0$, the relations $\bar{a}g=c\bar{e}$ and $ag/\bar{a}\bar{g}=ce/\bar{c}\bar{e}$ are obtained as reversible conditions, which are further simplified to the forms of $a=e$ and $c=g$ with the aid of the relation, $b\bar{g}=f\bar{c}$, which is expected for the reversible double Markovian process.

The relative intensities of *n*-ads for each case are summarized in Table V.

MICROSTRUCTURE OF POLY(METHYL PROPENYL ETHER)

The purpose of the present section is the NMR measurement and the analysis of the microstructure of cationically polymerized poly(methyl propenyl ether). An assignment in the NMR spectrum of the polymer has been reported by Higashimura and his colleague[3,4] where one (R.C.) of the authors is included. However, a new peak is found in this paper, so that a new assignment will be proposed here.

After preparation of the monomer and the catalysts, the polymerization was carried out in a similar manner to the method described by Ohsumi.[4] Characteristics of the polymers obtained with a homogeneous catalyst, $BF_3\cdot O(C_2H_5)_2$ are summarized in Table VI. Table VII is similar to the one for the polymers with heterogeneous catalysts such as the complex of sulfuric acid—aluminum sulfate.

Table VI. Characteristics of poly(methyl propenyl ether) with $BF_3\cdot O(C_2H_5)_2$[a]

Sample	*cis/trans* in monomer molar ratio	Polymerization		
		Solvent	Temp, °C	Conversion, %
BC-1	4 : 1	Toluene	−78	78
BC-2	4 : 1	Toluene	−40	65
BT-1	1 : 4	Toluene	−78	25
BM-1	3 : 2	Toluene	−78	23
BM-2	3 : 2	Toluene-CH_2Cl_2 (6 : 3)	−78	36
BM-3	3 : 2	Toluene-CH_2Cl_2 (1 : 8)	−78	47

[a] Conditions: $[M]_0$, 10 vol%; $[BF_3OEt_2]$, 4m mol/*l*.

Table VII. Characteristics of poly(methyl propenyl ether) with the complex of H_2SO_4—$Al_2(SO_4)_3$[a]

Sample	*cis/trans* in monomer molar ratio	Polymerization		
		Solvent	Temp, °C	Conversion, %
SC-1	4 : 1	Toluene	0	19
SC-2	4 : 1	Toluene	−22	13
SD-1	4 : 1	Toluene[b]	8	0.08[c]
SD-2	4 : 1	Toluene[b]	0	0.1[c]

[a] Conditions: $[M]_0$, 20 vol%; [complex], 0.4 g/100 m*l*. The composition of the complex: $Al_3(SO_4)_3\cdot 1.00\ H_2SO_4\ 4.46\ H_2O$.

[b] Solvent contains a trace of water.

[c] Conversions of methanol soluble parts: SD-1, 7.6%; SD-2, 15.5.

High resolution nuclear magnetic resonance (NMR) spectra of the polymers were measured with a JNM 4H-100 spectrometer operated at 100 MHz in a form of 5—10% (w/v) solution in *o*-dichlorobenzene. Spin decoupling was carried out by a sideband of 4 kHz. All spectra were measured at 160°C.

NMR spectra of the polymer are composed of the peaks from α-methoxyl protons ($\tau\simeq6.5$) overlapped with a broad peak from α-methynyl protons, the region from β-methynyl protons

($\tau \simeq 8.0$) and the region from β-methyl protons ($\tau \simeq 9.0$). β-Methynyl protons are thought to be coupled with both β-methyl and α-methynyl protons. Decoupling from β-methynyl protons, therfore, liberates β-methyl and α-methynyl protons from the coupling with β-methynyl ones. Hereafter, such decoupled spectra are denoted by $\beta \cdot \mathrm{C\underline{H}_3}$-{$\beta \mathrm{C\underline{H}}$} and $\alpha \mathrm{C\underline{H}}$-{$\beta \mathrm{C\underline{H}}$}, respectively. The latter is not so sharp to make it very difficult to obtain information from this region, but this informs us that the peaks from α-methoxyl protons (as previous mentioned overlap with those from α-methynyl) are not affected by the decoupling, so that we can analyze the spectra from methoxyl protons without consideration of coalescense with those from α-methynyl.

NMR Spectra of β-Methyl Protons

$\beta \mathrm{C\underline{H}}$-{$\beta \mathrm{C\underline{H}}$} spectra are composed of two peaks centered at 8.90 and 9.06 τ for all samples prepared with $\mathrm{BF_3 \cdot O(C_2H_5)_2}$ as shown in Figure 1. This fact means that there are two kinds of stereochemical configurations in these samples. Among them, the peak centered at 8.90 τ can be assigned to the (mM) (or *threo-meso*) configuration. Consequently, the sample BT-1 gives a more intensive peak at 8.90 τ than at 9.06 τ, and the X-ray diffraction pattern is very similar to that for *threo* di-isotropic poly(methyl propenyl ether) reported by Natta.[5] This assignment and its logic are the same as used by Ohsumi.[4]

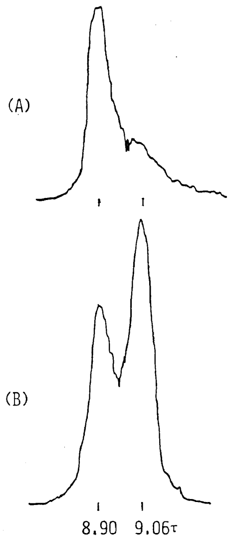


Figure 1. NMR spectra of β-methyl protons decoupled from β-methynyl proton: (A) BT-1; (B) BC-1.

Table VIII. Triad ditacticities from $\beta \mathrm{C\underline{H}_3}$—{$\beta \mathrm{C\underline{H}}$} spectra

Sample	(mM)	(mR)
BT-1	76.3%	23.7%
BM-3	60.4	39.6
BM-2	57.5	42.5
BC-2	52.9	47.1
BM-1	45.3	54.7
BC-1	40.7	59.3

The peak centered at 9.06 τ can be assigned to (mR) (or *racemic*) configuration. If this peak is assumed to originate from (rR) (or *erythro-meso*) configuration and the polymerization system obeys the reversible Markovian process, this system must be described by case 1 or 4. The *n*-ads due to methoxyl protons are composed of three kinds of structure, namely, (Mm), (Mr), and (Rr) in case 1, and (mMmM), (mMrR) and (rRrR) in case 4. To the contrary, the spectral of methoxyl protons are composed of four peaks at least as mentioned later, and therefore we must abandon the assumption. We then assign the peak centered at 9.06 τ to the (mR) configuration. This assignment is different from Ohsumi's. The difference is due to the difference in the operating frequencies of the spectrometers used.

The third ditacticities as tubulated in Table VIII were obtained by the intensities of $\beta \mathrm{C\underline{H}_3}$-{$\beta \mathrm{CH}$} spectra with the aid of the assignment in this paper.

NMR Spectra of Methoxyl Protons

Spectra from methoxyl protons do not split so clearly with each other as those from $\beta \mathrm{C\underline{H}_3}$-{$\beta \mathrm{CH}$}. Therefore, each component of the spectra must be decomposed by the assumption of suitable Lorentzian curves, if we wish to assign each peak precisely and to decide its intensity quantitatively. Four tops are observed in the region of methoxyl protons in every spectrum. Decomposition to four peaks making use of the information on four tops is reasonable. These four peaks are located at 6.44, 6.47, 7.48, and 6.50 τ after decomposition. A typical decomposition is reproduced in Figure 2. If the splitting is due to triad stereochemical configurations, we

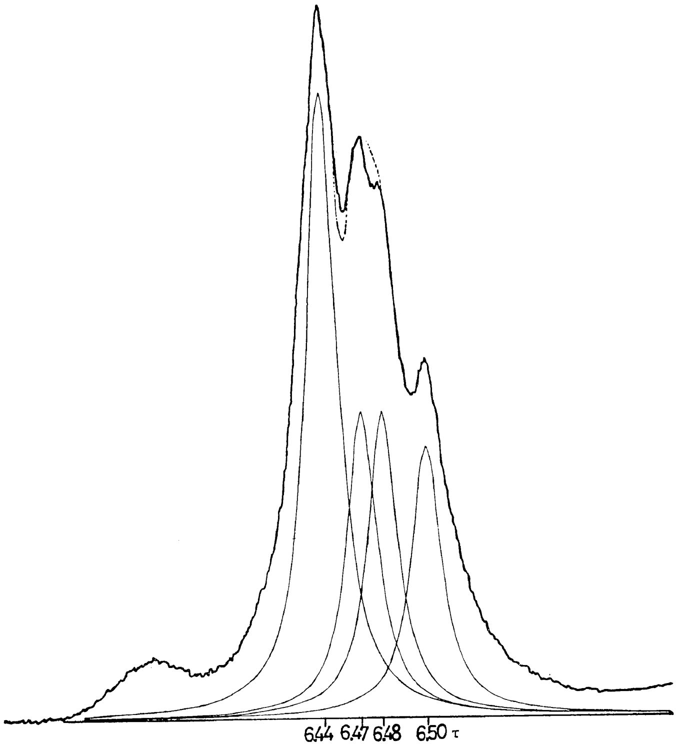


Figure 2. NMR spectrum of methoxyl protons: fine curves, Lorentzian curves; dotted lines, Decomposed curves of Lorentzian.

cannot expect a split into more than three peaks. Therefore, the splitting of the spectra is due to pentad stereochemical configurations.

The peak centered at 6.50 τ can be assigned the (mMmM) configuration because the sample BT-1, which is a *threo* diisotactic polymer as previously mentioned, shows the most intensive peak at this location.

The peaks centered at 6.47 and 6.48 τ always have the same intenfities as each other. For example, the normalized intensities are 20.3-% for both peaks at 6.47 and 6.48 τ. On the basis of this fact these two peaks are assigned as follows. We have the reduction relations between triads of β-methyl protons and pentads of methoxyl protons.

$$\begin{aligned}(\mathrm{mM}) &= (\mathrm{mMmM}) + \tfrac{1}{2}\{(\mathrm{mMmR}) + (\mathrm{mMrM}) + (\mathrm{mMrR})\}\\ (\mathrm{mR}) &= (\mathrm{mRmR}) + (\mathrm{mRrM}) + (\mathrm{rMmR}) + \tfrac{1}{2}\{(\mathrm{mMmR}) + (\mathrm{mMrM}) + (\mathrm{mRrR}) + (\mathrm{rMrR})\} \qquad (15)\\ (\mathrm{rR}) &= (\mathrm{rRrR}) + \tfrac{1}{2}\{(\mathrm{mMrR}) + (\mathrm{rMrR}) + (\mathrm{mRrR})\}\end{aligned}$$

The triad (rR) vanishes in the polymers obtained with $\mathrm{BF_3 \cdot (C_2H_5)_2}$ as previously mentioned. Then, eq 15 is simplified to

$$\begin{aligned}(\mathrm{mM}) &= (\mathrm{mMmM}) + \tfrac{1}{2}\{(\mathrm{mMmR}) + (\mathrm{mMrM})\}\\ (\mathrm{mR}) &= (\mathrm{mRmR}) + (\mathrm{mRrM}) + (\mathrm{rMmR}) + \tfrac{1}{2}\{(\mathrm{mMmR}) + (\mathrm{mMrM})\} \qquad (16)\end{aligned}$$

while the relations between the relative intensities of peaks can be found experimentally as

$$\left.\begin{aligned}(8.90\,\tau) &= (6.50\,\tau) + \tfrac{1}{2}\{(6.47\,\tau) + (6.48\,\tau)\}\\ (9.06\,\tau) &= (6.44\,\tau) + \tfrac{1}{2}\{(6.47\,\tau) + (6.48\,\tau)\}\end{aligned}\right\} \qquad (17)$$

From the comparison of eq 16 with eq 17, and the assignments (8.90 τ) : (mM) and (6.50 τ) : (mMmM), we have

$$(6.47\,\tau) + (6.48\,\tau) = (\mathrm{mMmR}) + (\mathrm{mMrM}) \qquad (18)$$

we cannot decide whether the peak centered at 6.47 τ is assigned to (mMmR) or (mMrM) at this stage, because the relative intensities of the peaks at 6.47 τ and 6.48 τ are equal to each other. However, the peaks centered at 6.47 and 6.48 τ can be assigned to (mMmR) and (mMmR) configurations, respectively, for the reason later described.

From the comparison of eq 16 with 17, we have the other relation

$$(6.44\,\tau)=(\mathrm{mRmR})+(\mathrm{mRrM})+(\mathrm{rMmR}) \quad (19)$$

However, it cannot be assumed that (mRrM) configuration is included in this peak because the samples polymerized with sulfuric acid—aluminum sulfate complex show the other peak centered at 6.55 τ besides the peaks above mentioned as shown in Figure 3. The intensity of this peak increases with that of a doublet (8.81 and 8.875 τ) in β-methyl region, which may be assigned to (Rr), while the intensity of 6.50 τ which is already assigned to (Mm), increases with that of a doublet (8.85 and 8.92 τ). Then, the peak at 6.55 τ is assigned to (Rr), so that the peak at 6.44 τ does not include this configuration. As a result, three possibilities remain for the assignment of the peak at 6.44 τ, namely, (1) (mRmR), (2) (rMmR), and (3) (mRmR)+(rMmR). If the assignment 2 is adopted, the structures [mMrM] and [mRmM] must exist always before and after the structure [rMmR], respectively. This requires the relation, (rMmR)<(mMrM). This contradicts with an experimental finding, (6.44 τ)>(6.47 τ). Next, the relations

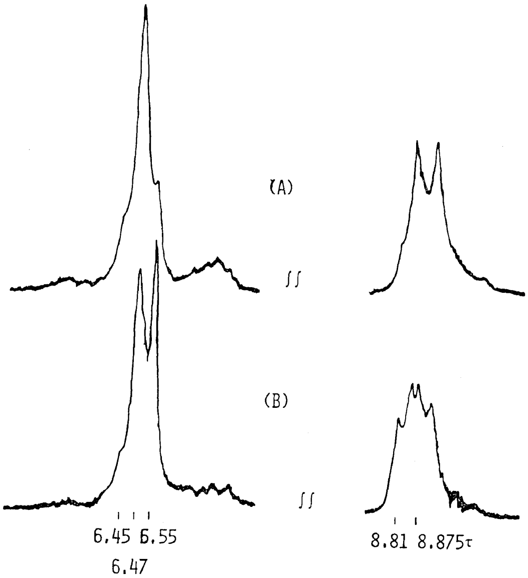


Figure 3. NMR spectra of PMPE obtained by $Al_2(SO_4)_3 \cdot H_2SO_4$ complex in toluene: (A) SD-1, prepared at 8°C; (B) SD-2, prepared at 0°C.

$$\begin{aligned}[\mathrm{mM}]&=[\mathrm{mMm}]+[\mathrm{mMr}]\\&=[\mathrm{mMmM}]+[\mathrm{mMmR}]+[\mathrm{mMrM}]\\&\quad+[\mathrm{mMrR}] \qquad (20)\\&=[\mathrm{MmM}]+[\mathrm{RmM}]\\&=[\mathrm{mMmM}]+[\mathrm{rMmM}]+[\mathrm{mRmM}]\\&\quad+[\mathrm{rRmM}] \qquad (21)\\[\mathrm{mR}]&=[\mathrm{mRm}]+[\mathrm{mRr}]\\&=[\mathrm{mRmM}]+[\mathrm{mRmR}]+[\mathrm{mRrM}]\\&\quad+[\mathrm{mRrR}] \qquad (22)\\&=[\mathrm{MmR}]+[\mathrm{RmR}]\\&=[\mathrm{mMmR}]+[\mathrm{rMmR}]+[\mathrm{mRmR}]\\&\quad+[\mathrm{rRmR}] \qquad (23)\end{aligned}$$

between triads and pentads are considered. By a condition of [rR]+[Rr]=0, eq 20 and 21 are reduced to

$$[\mathrm{mRmM}]+[\mathrm{rMmM}]=[\mathrm{mMmR}]+[\mathrm{mMrM}] \quad (24)$$

Similarly, eq 22 and 23 are reduced to

$$[\mathrm{mRmM}]=[\mathrm{mMmR}]+[\mathrm{rMmR}] \quad (25)$$

By the consideration of an experimental finding, (6.47 τ)=(6.48 τ), eq 24 and 25 are further reduced to

$$[\mathrm{rMmR}]=(\mathrm{rMmR})=0 \quad (26)$$

Therefore, the assignment 3 must be also abandoned and the peak centered at 6.44 can be assigned to (mRmR).

NMR Spectra of β-Methynyl Protons

NMR spectra of β-methynyl protons are so broad as shown in Figure 4 that the assignments of them are rather difficult. However, we can say qualitatively that the polymers obtained with $BF_3 \cdot O(C_2H_5)_2$ show rather broad peaks at 7.95 τ and the intensities and the chemical shifts are insensitive to the ditacticity of the polymers. This is analogous to an experimental finding for NMR spectra of poly(methyl vinyl ether),[6] namely, the chemical shifts between the *racemic* and *meso* (*threo* or *erythro*) configurations of

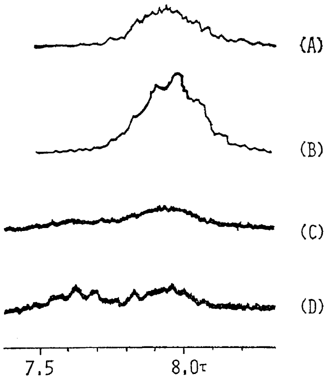


Figure 4. NMR spectra of β-methynyl proton: (A) BT-1; (B) BC-1; (C) SD-1; (D) SD-2.

methylenic protons coincide with each other. The other peak at 7.7 τ is observed in the polymer obtained with sulfuric acid—aluminum sulfate complex, and this peak grows with the increase in *erythro-meso* configuration. We can then assign the peak centered at 7.7 τ as *erythro-meso* and the peak at 7.95 τ as *threo-meso* and *racemic.* This behavior suggests that in the AB quartet of methylenic protons in poly(methyl vinyl ether) *erythro-meso* appears at the lower τ-value and *threo-meso* appears at the higher τ-value. Such analogous behavior between methylenic protons in poly(methyl vinyl ether) and methynil protons in poly(methyl propenyl ether) causes us to consider the similarity of NMR spectra between methoxyl protons in both polymers. This is the reason why the (mRrM) configuration is excluded from the assignment to 6.44 τ in the last section. The assignment of (mMmR) to 6.48 τ is also made for the same reason because the difference in chemical shifts between isotactic and heterotactic triads in poly(methyl vinyl ether) is 0.02 τ so that we can expect the peak for (mMmR) configuration to be lower than for (mMmR) by 0.02 τ.

In conclusion, we assign the NMR spectra of poly(methyl propenyl ether) as follows

6.44 τ: (rMrM)
6.47 τ: (mMrM)
6.48 τ: (mMmR)
6.50 τ: (mMmM)
methoxyl protons

7.7 τ: (rR)
7.95 τ: (mM)+(mR)
β-methynyl protons

8.90 τ: (mM)
9.06 τ: (mR)
β-methyl protons

POLYMERIZATION MECHANISM OF METHYL PROPENYL ETHER

In this section the polymerization mechanism is considered for the system of *cis*-methyl propenyl ether with $BF_3 \cdot O(C_2H_5)_2$ according to the NMR spectra and their assignments described in the previous section.

According to an experimental finding in the last section, we can have two kinds of model for the polymer. One of them is

(A) [mMmR]=[mRmR]=[mRmM]=0

The other model is the reverse of (A), *i.e.*,

(B) [mMrM]=[rMrM]=[rMmM]=0

In the model A there is no existing [R] structure, and both of structures [m] and [r] exist in the polymer. It can them be assumed that adding monomers always open in *trans* form, but the attacks on monomers are random. On the other hand, model B leads to the absence of [r] and the existence of both structures of [M] and [R]. It can be assumed in this case that adding monomers open randomly, but the attacks on monomers are limited to the finding that the β-methyl groups in adding monomers are always taken into *meso* form with respect to the methoxyl groups in growing ends. To establish further confirmation of these findings will be a problem for the future.

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REFERENCES

1. G. Natta, M. Farina, M. Peraldo, P. Corradini, G. Bressan, and P. Ganis, *Rend. Accad. Naz. Lincei*, **28**, 442 (1960).
2. H. L. Frisch, C. L. Mallows, and F. A. Bovey, *J. Chem. Phys.*, **45**, 1565 (1966).
3. T. Higashimura, S. Kusudo, Y. Ohsumi, A.

Mizote, and S. Okamura, *J. Polym. Sci. Part A-1*, **6**, 2511 (1968).
4. Y. Ohsumi, T. Higashimura, S. Okamura, R. Chûjô, and T. Kuroda, *J. Polym. Sci.*, *Part A-1*, **5**, 3009 (1967).
5. G. Natta and F. Danusso, "Stereoregular Polymers and Stereospecific Polymerizations," Pergamon Press, Oxford, 1967.
6. F. A. Bovey, E. W. Anderson, D. C. Douglass, and J.A. Manson, *J. Chem. Phys.*, **39**, 1199 (1963).