Copolymer Sequence Distribution with Chiral Stereoregularity and Its Application to Poly(acrylonitrile-*co*-methacrylonitrile)

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ABSTRACT: An attempt was made to elucidate the general mathematical expression of the polymer sequence distribution for copolymers with two stereoregular monomer units by considering their chirality (D or L form) distribution based on Markov statistics. The equations derived (DL equations) were compared with those based on conventional *meso* and *racemo* conformation (*mr* equations) [K. Kamide and K. Hisatani, *Polym. J.*, **24**, 1377 (1992)]. For this purpose the literature data of NMR on sequence distribution of three kinds of poly(acrylonitrile-*co*-methacrylonitrile) *i.e.*, poly(AN-*co*-MAN), prepared by radical polymerization using redox catalysis and anionic method using dialkylmagnesium as initiator at high and low temperature, were analyzed. DL equations were found to explain well the monomer unit sequence distribution with cotacticity of two poly(AN-*co*-MAN), polymerized by radical method and by anionic methods at temperatures, rather than *mr* equations. The reaction probability of these copolymers estimated by [Bernoulli] $-$ [1st Markov]$_{cor}$ statistics where monomer unit sequence and its cotacticity obey Bernoulli and 1st order Markov processes, respectively, has revealed that *racemo* addition of MAN monomer does not occur in the above anionic polymerization essentially. For all of three samples, the stereoregular sequences obey 1st order Markov statistics, but monomer unit ones obey 2nd order Markov statistics for low temperature anionic method and Bernoulli for the other two method.

KEY WORDS   Copolymer Sequence Distribution / DL Type Conformational Sequence / Poly(acrylonitrile-*co*-methacrylonitrile) / ^{13}C NMR Spectrometer / Bernoulli Statistics / Markov Statistics / Triad Sequence /

Sequence distribution combined with stereoregularity of homo- and copolymeric chains, which is determined by polymerization mechanism, is a very important factor in governing the dissolved state of the polymers in solution, the solution properties, the structure and properties of the polymer solid. The most powerful experimental tool to determine the sequence distribution is nuclear magnetic resonance (NMR). But NMR often gives information on the diad-base sequence distribution of many polymers, that is *meso* or *racemo* (*m* or *r*) conformation for homo- and copolymers. The *mr* expression might be adequate to describe the sequence distribution combined with stereoregularity if the direction of the sequence of molecular chain for the homo- or copolymer in question can be completely neglected. Lots of studies on sequence distribution of homo- and copolymers based on the *mr* expression have been reported from the early works made by Frisch *et al.*[1] and Bovey.[2] The *m* or *r* diad sequence, however, essentially arises from the result of reaction of monomers with their chirality, D or L in the polymerization process. For example, an r diad includes a DL or LD sequence, and if the direction of the sequence cannot be ignored DL and LD diads should be distinguished. Consequently, NMR data on the sequence distribution had better to be analyzed using a statistical model described by D and L sequence parameters as far as possible. On this background, the theoretical calculations on D and L sequences (DL sequences) of homopolymers (such as poly(methyl methacrylate)) were intensively carried out based on Bernoulli and 1st order Markov statistics mainly in 1960s.[3-9] But, the application of the calculation methods to the existing homopolymers was substantially impossible due to the low resolving power of NMR at that time. Subsequent progress on NMR measurement

has made it possible to apply the statistical model for homopolymers, based on the DL sequence as proposed by Shuerch,[3] Fueno,[5] and Chujo *et al.*[8,9]

DL sequence expression might be expanded to describe the sequence distribution combined with stereoregularity for copolymers, in which at least one of monomer units has stereoregularity. For this class of copolymers, we have already made several attempts to calculate the monomer unit sequence and cotacticity on the basis of the *mr* expression.[10,11] We have dealt with the cases where the monomer unit sequence distribution (MSD) and its cotacticity (CTD) statistically correlated with each other or not. Kamide and Hisatani[10] and Hisatani *et al.*[11] statistically calculated the *mr* sequence of copolymer on the basis of strict Markov statistics. Kamide and Hisatani analyzed NMR data of poly(acrylonitrile(AN)-*co*-methacrylonitrile(MAN)), prepared by three different polymerization methods, reporting that *mr* sequence fractions of poly (AN-*co*-MAN), polymerized using anionic initiator at high temperature considerably deviated from the calculated results. This deviation of the *mr* sequence fractions from the experimental data is possibly due to the use of a statistical model based on the *mr* sequence. In other words, the deviation might be brought about by the co-ordination polymerization mechanism employing dialkylmagnesium at temperatures above 100°C reported by Ono *et al.*,[12-15] in which mechanism polymeric chain direction cannot be ignored. In this study, an attempt was made to derive basic equations describing the monomer unit sequence with its cotacticity of copolymers, consisting of two kinds of monomers on the basis of DL sequence statistics as an extension of previous works[10,11] and to apply the equations to experimental data of ^{13}C NMR of poly-(AN-*co*-MAN) obtained by radical and anionic polym-

erization methods reported in the literature.[10]

THEORETICAL BACKGROUND

Statistical Models of Copolymer Sequence with DL Stereoregularity

Now we consider the case where monomer unit sequence of copolymer with two kinds of monomers (A and B) obeys Bernoulli, the 1st, and the 2nd order Markov statistics and each of the two monomers possesses possibility to yield stereoregular homopolymers (*e.g.*, AAA$\cdots$AA and BBB$\cdots$BB), as assumed in the previous paper.[8] Then the chirality distribution (CHD) of the copolymer should be also described by the three kinds of Markov statistics. There are two cases for such copolymer when the statistics on MSD and its CHD are independent and correlative to each other. Hereafter, the statistical model is, for example, represented as [1st Markov] $-$ [Bernoulli]$_{ind(cor)}$, when the MSD and its CHD obey independently (correlatively) the 1st order Markov and Bernoulli statistics, respectively. Statistical models based on *mr* and *DL* sequence will be referred to as *mr* and *DL* models, respectively.

Independent Statistical Model

The molar fraction of each sequence is expressed by the product of those of monomer unit and its chirality sequential part, because both sequences are independent of each other, obeying Bernoulli, the 1st or the 2nd order Markov statistics. As an example of calculation results of the independent statistical models, we show the molar fractions of triad *mr* sequences calculated on the basis of [1st Markov] $-$ [Bernoulli]$_{ind}$. The triad *mr* sequences are expressed by six kinds of probability variables, amongst which the following relations are held:

$$P_{(A/A)} + P_{(B/A)} = 1 \tag{1a}$$

$$P_{(A/B)} + P_{(B/B)} = 1 \tag{1b}$$

$$P_L + P_D = 1 \tag{1c}$$

Here, for example, $P_{(B/A)}$ is the probability for B to add to an A end and P_L is one for L form monomer to add to arbitrary monomer unit end. In this model, three probability variables are independent from each other. In other words, if the values of three probability variables are determined, this statistical model is completely described.

If we show monomer unit A in the D form as A_D and replace $P_{(A/B)} + P_{(B/A)}$ by $D^{2M(1)}$ which indicates a two-monomer system (2M) with 1st order Markov process (1), then some triad *mr* sequence fractions out of totally 20 kinds, are able to be written as follows:

$$(A^mA^mA) = (P_D^3 + P_L^3)P_{(A/A)}^2 P_{(A/B)}/D^{2M(1)} \tag{2a}$$

$$(A^mA^rB) = 2P_D P_L P_{(A/A)} P_{(B/A)} P_{(A/B)}/D^{2M(1)} \tag{2b}$$

$$(A^mB^rA) = 2P_D P_L P_{(B/A)} P_{(A/B)}^2/D^{2M(1)} \tag{2c}$$

$$(A^rB^mB) = 2P_D P_L P_{(B/B)} P_{(B/A)} P_{(A/B)}/D^{2M(1)} \tag{2d}$$

$$(B^mB^rB) = 2P_D P_L P_{(B/B)}^2 P_{(B/A)}/D^{2M(1)} \tag{2e}$$

$$(B^rB^rB) = P_D P_L P_{(B/B)} 2P_{(B/A)}/D^{2M(1)} \tag{2f}$$

where superscripts *m* and *r* mean *comeso* and *coracemo* conformation, respectively.

Correlative Statistical Model

[*Bernoulli*] $-$ [*Bernoulli*]$_{cor}$

The probability parameters which describe the *mr* sequence on this model relate with each other through the following equation:

$$P_{AD} + P_{AL} + P_{BD} + P_{BL} = 1 \tag{3}$$

where P_{AD} is the probability for A with D form to add to the propagating end, irrespective of the chemical species or the chirality of the end, where $P_{AD} + P_{AL} = P_A$ and $P_{BD} + P_{BL} = P_B$ are satisfied in the case. The molar fractions of all triad *mr* sequences are calculated as follows:

$$(A^mA^mA) = P_{AD}^3 + P_{AL}^3 = P_A(P_{AD}^2 - P_{AD}P_{AL} + P_{AL}^2) \tag{4a}$$

$$(A^mA^rA) = 2P_{AD}P_{AL}(P_{AD} + P_{AL}) = 2P_A P_{AD}P_{AL} \tag{4b}$$

$$(A^rA^rA) = P_{AD}P_{AL}(P_{AD} + P_{AL}) = P_A P_{AD}P_{AL} \tag{4c}$$

$$(A^mA^mB) = 2(P_{AD}^2 P_{BD} + P_{AL}^2 P_{BL}) \tag{5a}$$

$$(A^mA^rB) = 2(P_{AD}^2 P_{BL} + P_{AL}^2 P_{BD}) \tag{5b}$$

$$(A^rA^mB) = 2P_{AD}P_{AL}(P_{BD} + P_{BL}) = 2P_B P_{AD}P_{AL} \tag{5c}$$

$$(A^rA^rB) = 2P_{AD}P_{AL}(P_{BD} + P_{BL}) = 2P_B P_{AD}P_{AL} \tag{5d}$$

$$(B^mA^mB) = P_{AD}P_{BD}^2 + P_{AL}P_{BL}^2 \tag{6a}$$

$$(B^mA^rB) = 2(P_{AD} + P_{AL})P_{BD}P_{BL} = 2P_A P_{BD}P_{BL} \tag{6b}$$

$$(B^rA^rB) = P_{AL}P_{BD}^2 + P_{AD}P_{BL}^2 \tag{6c}$$

$$(A^mB^mA) = P_{AD}^2 P_{BD} + P_{AL}^2 P_{BL} \tag{7a}$$

$$(A^mB^rA) = 2P_{AD}P_{AL}(P_{BD} + P_{BL}) = 2P_B P_{AD}P_{AL} \tag{7b}$$

$$(A^rB^rA) = P_{AD}^2 P_{BL} + P_{AL}^2 P_{BD} \tag{7c}$$

$$(A^mB^mB) = 2(P_{AD}P_{BD}^2 + P_{AL}P_{BL}^2) \tag{8a}$$

$$(A^mB^rB) = 2(P_{AD} + P_{AL})P_{BD}P_{BL} = 2P_A P_{BD}P_{BL} \tag{8b}$$

$$(A^rB^mB) = 2(P_{AL}P_{BD}^2 + P_{AD}P_{BL}^2) \tag{8c}$$

$$(A^rB^rB) = 2(P_{AD} + P_{AL})P_{BD}P_{BL} = 2P_A P_{BD}P_{BL} \tag{8d}$$

$$(B^mB^mB) = P_{BD}^3 + P_{BL}^3 = P_B(P_{BD}^2 - P_{BD}P_{BL} + P_{BL}^2) \tag{9a}$$

$$(B^mB^rB) = 2P_{BD}P_{BL}(P_{BD} + P_{BL}) = 2P_B P_{BD}P_{BL} \tag{9b}$$

$$(B^rB^rB) = P_{BD}P_{BL}(P_{BD} + P_{BL}) = P_B P_{BD}P_{BL} \tag{9c}$$

[*Bernoulli*] $-$ [*1st Markov*]$_{cor}$

This model is expressed by eight probability variables and relationships among them are as follows:

$$P_{(AD/D)} + P_{(AL/D)} + P_{(BD/D)} + P_{(BL/D)} = 1 \tag{10a}$$

$$P_{(AD/L)} + P_{(AL/L)} + P_{(BD/L)} + P_{(BL/L)} = 1 \tag{10b}$$

Here, $P_{(AD/D)}$, for example, means the probability for A with D form adding to the arbitrary propagating end with the D form of either A or B unit. As is easily shown, six variables are independent. Two equations, $P_{(AL/D)} + P_{(BL/D)} = P_{(L/D)}$ and $P_{(AD/L)} + P_{(BD/L)} = P_{(D/L)}$ also hold in the model. The sums of probabilities ($P_{(AL/D)}$, $P_{(BL/D)}$, $P_{(AD/L)}$, $P_{(BD/L)}$) and ($P_{(L/D)}$, $P_{(D/L)}$) are written as $D^{DL(1)}$, which is a characteristic parameter of this statistical model:

$$P_{(AL/D)} + P_{(BL/D)} + P_{(AD/L)} + P_{(BD/L)} = P_{(L/D)} + P_{(D/L)} = D^{DL(1)} \tag{11}$$

$P_{(D/L)}$, $P_{(L/D)}$ and the eight parameters in eq 10a, b satisfy the following equations, (12a, b) and (13a—d):

$$D_{AD}^{DL} + D_{BD}^{DL} = P_{(D/L)} \tag{12a}$$

$$D_{AL}^{DL} + D_{BL}^{DL} P_{(L/D)} \tag{12b}$$

where D_{AD}^{DL}, D_{AL}^{DL}, D_{AD}^{DL}, and D_{BL}^{DL} and D_{BL}^{DL} are defined as the following relations:

$$D_{AD}^{DL} = P_{(AD/D)}P_{(D/L)} + P_{(AD/L)}P_{(L/D)} \tag{13a}$$

$$D_{AL}^{DL} = P_{(AL/D)}P_{(D/L)} + P_{(AL/L)}P_{(L/D)} \tag{13b}$$

$$D_{BD}^{DL} = P_{(BD/D)}P_{(D/L)} + P_{(BD/L)}P_{(L/D)} \tag{13c}$$

$$D_{BL}^{DL} = P_{(BL/D)}P_{(D/L)} + P_{(BL/L)}P_{(L/D)} \tag{13d}$$

The three typical triad mr sequences are written using probability parameters as follows:

$$(A^mA^mA) = (P_{(AD/D)}^2, \ D_{AD}^{DL} + P_{(AL/L)}^2)/D^{DL(1)} \tag{14a}$$

$$(A^mA^rA) = (P_{(AD/D)} + P_{(AL/L)})(P_{(AL/D)}D_{AD}^{DL} + P_{(AD/L)}D_{AL}^{DL})/D^{DL(1)} \tag{14b}$$

$$\begin{aligned}(A^rA^rA) &= P_{(AL/D)}P_{(AD/L)}(D_{AD}^{DL} + D_{AL}^{DL})/D^{DL(1)} \\ &= P_{(AL/D)}P_{(AD/L)}(P_{(A/L)}P_{(L/D)} \\ &\quad + P_{(A/D)}P_{(D/L)})/D^{DL(1)} \end{aligned} \tag{14c}$$

The other seventeen triad fractions are indicated in Appendix A.

[1st Markov] − [Bernoulli]$_{cor}$

This model also consists of eight probability variables, and the relationships among them are indicated by the following equations:

$$P_{(AD/A)} + P_{(AL/A)} + P_{(BD/A)} + P_{(BL/A)} = 1 \tag{15a}$$

$$P_{(AD/B)} + P_{(AL/B)} + P_{(BD/B)} + P_{(BL/B)} = 1 \tag{15b}$$

Consequently, six variables are independent of each other. $D^{2M(1)}$ is defined as a sum of four probability variables:

$$\begin{aligned}D^{2M(1)} &= P_{(AD/B)} + P_{(AL/B)} + P_{(BD/A)} + P_{(BL/A)} \\ &= P_{(B/A)} + P_{(A/B)} \end{aligned} \tag{16}$$

The typical triad mr sequences are written using probability parameters as follows:

$$(A^mA^mA) = (P_{(AD/A)}^2 D_{AD}^{2M} + P_{(AL/A)}^2 D_{AL}^{2M})/D^{2M(1)} \tag{17a}$$

$$\begin{aligned}(A^mA^rA) &= \{P_{(AD/A)}P_{(AL/A)}D_{AD}^{2M} + D_{AL}^{2M}) + P_{(AL/A)}^2 D_{AD}^{2M} \\ &\quad + P_{(AD/D)}^2\}D_{AL}^{2M}\}D^{2M(1)} \end{aligned} \tag{17b}$$

$$\begin{aligned}(A^rA^rA) &= P_{(AL/A)}P_{(AD/A)}(D_{AD}^{2M} + D_{AL}^{2M})/D^{2M(1)} \\ &= P_{(A/B)}P_{(AL/A)}P_{(AD/A)}/D^{2M(1)} \end{aligned} \tag{17c}$$

Here, D_{AD}^{2M}, D_{AL}^{2M}, D_{BD}^{2M}, and $D_{BL}^{2M} =$ are defined as follows:

$$D_{AD}^{2M} = P_{(AD/A)}P_{(A/B)} + P_{(AD/B)}P_{(B/A)} \tag{18a}$$

$$D_{AL}^{2M} = P_{(AL/A)}P_{(A/B)} + P_{(AL/B)}P_{(B/A)} \tag{18b}$$

$$D_{BD}^{2M} = P_{(BD/A)}P_{(A/B)} + P_{(BD/B)}P_{(B/A)} \tag{18c}$$

$$D_{BL}^{2M} = P_{(BL/A)}P_{(A/B)} + P_{(BL/B)}P_{(B/A)} \tag{18d}$$

The other seventeen triad molar fractions are to be indicated in Appendix B.

Method to Determine the Most Probable Model

The method to select the most suitable statistics is the same as that already described in ref 10 and 11, using eq 19.

Table I(a). Comparison of values of parameter δ'_{min} between DL- and mr-type statistics on sample AMN3

Sample code	Statistics			$\delta'_{min} \times 1000$	
	Correlative/ independent	Monomere unit sequence	Cotacticity/ chirality	DL-Type	mr-Type
RMN3	Independent	Bernoulli	Bernoulli	3.46	2.75
		Bernoulli	1st Markov	2.75	2.70
		Bernoulli	2nd Markov	2.70	2.70
		1st Markov	Bernoulli	1.83	1.70
		1st Markov	1st Markov	1.69	1.69
		1st Markov	2nd Markov	1.69	1.69
		2nd Markov	Bernoulli	1.12	0.98[a]
		2nd Markov	1st Markov	0.97	0.97
		2nd Markov	2nd Markov	0.97	0.97
	Correlative	Bernoulli	Bernoulli	2.74	2.27
		Bernoulli	1st Markov	0.83	1.04
		1st Markov	Bernoulli	1.31	1.32
		σ-Parameter model		—	2.01

[a] Underline, the most suitable statistics.

$$\delta' = \frac{\sqrt{\sum_{i=1}^{N}(X_i - Y_i)^2}}{N} \tag{19}$$

where X_i and Y_i are the experimental and calculated molar fractions for a specific heptad sequence, respectively, and N is the total number of heptad sequences which can be distinguishable from others in an NMR spectrum even if there are any overlapping peaks. This δ'-method is completed by itself, but it is better in general to reconfirm or check the suitability of the statistical model through the use of other independent method especially when the number of model parameters is large.

RESULTS AND DISCUSSION

Poly (acrylonitrile-co-methacrylonitrile)

The values of δ'_{min} (the minimum value of δ' in eq 19) of the poly (AN-co-MAN), prepared by the radical polymerization method (sample code RMN3 in ref 10) and synthesized using dialkylmagnesium as initiator at $-77°C$ (AMN2) and $120°C$ (AMN3)[10] were numerically calculated using triad sequence fractions, experimentally determined for each polymer (see Tables Ia—c). In the tables, δ'_{min} obtained by the mr model is also listed for comparison. If we analyze the experimental data of the sample RMN3 based on the independent mr model (Table Ia), δ'_{min} monotonically decreases substantially depending on the order of Markov statistics on MSD. On the other hand, δ'_{min} calculated on the basis of the independent DL model depends on the order of Markov statistics on cotacticity as well as monomer unit sequence. The most suitable model which gives the lowest δ'_{min} value (0.83) is [Bernoulli] − [1st Markov]$_{cor}$ based on the DL model for this polymer. This suggests that the chirality of the active end controls the reactive behavior of the monomer in the radical polymerization.

For the sample AMN2, [2nd Markov] − [1st or 2nd Markov]$_{ind}$ gives the lowest δ'_{min} value (2.3$_1$), irrespective of the type of sequence, as shown in Table Ib. Re-

Sequence Distribution of Poly(AN-co-MAN)

Table I(b). Comparison of values of parameter δ'_{min} between DL- and mr-type statistics on sample AMN2

Sample code	Correlative/ independent	Monomere unit sequence	Cotacticity/ chirality	$\delta'_{min} \times 1000$ DL-Type	mr-Type
		Bernoulli	Bernoulli	6.90	8.14
		Bernoulli	1st Markov	6.86	6.86
		Bernoulli	2nd Markov	6.86	6.86
		1st Markov	Bernoulli	6.87	5.45
	Independent	1st Markov	1st Markov	3.33	3.33
		1st Markov	2nd Markov	3.33	3.33
AMN2		2nd Markov	Bernoulli	6.21	4.89
		2nd Markov	1st Markov	2.31	2.81[a]
		2nd Markov	2nd Markov	2.31	2.31
		Bernoulli	Bernoulli	6.81	7.87
	Correlative	Bernoulli	1st Markov	7.31	6.58
		1st Markov	Bernoulli	2.71	5.19
		σ-Parameter model		—	4.30

[a] Underline, the most suitable statistics.

Table I(c). Comparison of values of parameter δ'_{min} between DL- and mr-type statistics on sample AMN3

Sample code	Correlative/ independent	Monomere unit sequence	Cotacticity/ chirality	$\delta'_{min} \times 1000$ DL-Type	mr-Type
		Bernoulli	Bernoulli	10.04	14.21
		Bernoulli	1st Markov	9.14	9.14
		Bernoulli	2nd Markov	9.14	9.14
		1st Markov	Bernoulli	9.08	13.49
	Independent	1st Markov	1st Markov	8.15	8.15
		1st Markov	2nd Markov	8.15	8.15
AMN3		2nd Markov	Bernoulli	8.88	13.43
		2nd Markov	1st Markov	7.80	7.80
		2nd Markov	2nd Markov	7.80	7.80
		Bernoulli	Bernoulli	6.84	12.23
	Correlative	Bernoulli	1st Markov	3.37	4.88[a]
		1st Markov	Bernoulli	4.88	11.22
		σ-Parameter model		—	6.65

[a] Underline, the most suitable statistics.

Table II. Values of statistical parameters of the most suitable statistics for DL- and mr-type on each poly(acrylonitrie-co-methacylonitrile) sample

Sample code	DL-Type The most suitable statistics	Parameter		mr-Type The most suitable statistics	Parameter	
RMN3	[Bernoulli] − [1st Markov]$_{cor}$	$P_{(AD/D)}$ 0.183$_9$ $P_{(AL/D)}$ 0.547$_1$ $P_{(MD/D)}$ 0.000$_0$ $P_{(ML/D)}$ 0.269$_0$ $P_{(AD/L)}$ 0.053$_7$ $P_{(AL/L)}$ 0.269$_3$ $P_{(MD/L)}$ 0.277$_5$ $P_{(ML/L)}$ 0.399$_5$	0.270$_3$ 0.052$_2$ 0.399$_1$ 0.278$_5$ 0.539$_1$ 0.194$_1$ 0.269$_8$ 0.000$_0$	[2nd Markov] − [Bernoulli]$_{ind}$	$P_{(A/AA)}$ 0.347$_6$ $P_{(A/AM)}$ 0.486$_5$ $P_{(A/MA)}$ 0.420$_4$ $P_{(A/MM)}$ 0.454$_5$ P_m 0.537$_4$	
AMN2	[2nd Markov] − [1st Markov]$_{ind}$	$P_{(A/AA)}$ 0.853$_4$ $P_{(A/AM)}$ 0.972$_8$ $P_{(A/MA)}$ 0.667$_5$ $P_{(A/MM)}$ 0.454$_1$ $P_{(L/D)}$ 0.334$_2$ $P_{(D/L)}$ 0.688$_0$		[2nd Markov] − [1st Markov]$_{ind}$	$P_{(A/AA)}$ 0.854$_1$ $P_{(A/AM)}$ 0.963$_9$ $P_{(A/MA)}$ 0.668$_1$ $P_{(A/MM)}$ 0.454$_8$ $P_{(r/m)}$ 0.399$_5$ $P_{(m/r)}$ 0.489$_1$	
AMN3	[Bernoulli] − [1st Markov]$_{cor}$	$P_{(AD/D)}$ 0.678$_7$ $P_{(AL/D)}$ 0.280$_3$ $P_{(MD/D)}$ 0.041$_0$ $P_{(ML/D)}$ 0.000$_0$ $P_{(AD/L)}$ 0.616$_3$ $P_{(AL/L)}$ 0.000$_0$ $P_{(MD/L)}$ 0.027$_4$ $P_{(ML/L)}$ 0.356$_3$	0.000$_0$ 0.637$_8$ 0.362$_2$ 0.000$_0$ 0.271$_1$ 0.681$_6$ 0.000$_0$ 0.047$_3$	[Bernoulli] − [1st markov]$_{cor}$	$P_{(mA/m)}$ 0.670$_4$ $P_{(rA/m)}$ 0.222$_1$ $P_{(mM/m)}$ 0.001$_7$ $P_{(rM/m)}$ 0.105$_8$ $P_{(mA/r)}$ 0.338$_2$ $P_{(rA/r)}$ 0.515$_0$ $P_{(mM/r)}$ 0.146$_8$ $P_{(rM/r)}$ 0.000$_0$	

garding the sample AMN3, the most suitable statistics to represent the monomer and cotacticity sequence is [Bernoulli] − [1st Markov]$_{cor}$ ($\delta'_{min} = 3.37 \times 10^{-3}$), based on the DL model (Table Ic). δ'_{min} value for AMN3 is fairly large, compared with those of other two copolymers under the most probable statistical combination. This might arise from the fact that the side reaction takes place relatively largely for anionic copolymerization, as the same as homopolymerization of AN proved previously,[16] leading to somewhat error for NMR analysis.

In Table II, the probability parameters which give the least δ'_{min} based on the mr and DL models for each

polymer are listed. In the case of the sample RMN3, the probability parameters of [2nd Markov] − [Bernoulli]$_{ind}$, based on the mr model are representatively listed. The DL model for the samples RMN3 and AMN3 gives two series of the probability parameters (P and Q) as a solution of eq 19 for one value of δ'_{min} (fourth and fifhth column of the table). As exemplified by the case when the value of $P_{(AL/D)}$ for the sample RMN3 in the fourth column (0.54$_7$) is very close to the value of $P_{(AD/L)}$ in the fifth column (0.53$_9$), the value of a parameter P for the monomer AN or MAN belonging to one group is almost equal to that of the parameter Q in the other group,

where each of P and Q corresponds to a parameter substitution of D and L for L and D, respectively. This seems closely relevant to the fact that the two groups of parameters attribute to the same phenomenon substantially, considering that D and L forms of the both monomer are in reflecting image relation.

The probability parameters of both monomers (AN and MAN), obtained by the mr model for the sample RMN3 are almost moderate values (0.35—0.49). But those obtained by the DL model show significant dependence on addition manners of the monomers. For example, the probability of occurrence of $meso$ addition of MAN ($P_{(ML/L)}$ and $P_{(MD/D)}$) takes two extreme values, about 0.4 and zero, while the probability of $racemo$ addition ($P_{(ML/D)}$ and $P_{(MD/L)}$) is about 0.27. This value is very near to 0.25, which does not seem to have any characteristic significance.

The probability parameters $P_{(L/D)}$ and $P_{(D/L)}$ of the DL model are related to the complicated parameters with monomer unit, such as $P_{(AL/D)}$, through the following equations:

$$P_{(L/D)} = P_{(AL/D)} + P_{(ML/D)} \qquad (20a)$$

$$P_{(D/L)} = P_{(AD/L)} + P_{(MD/L)} \qquad (20b)$$

By substitution of the values of the parameters in the fourth and fifth columns for the sample RMN3 into the right-hand-side of both equations we obtain $P_{(L/D)} = 0.81_6$, $P_{(D/L)} = 0.33_1$ and $P_{(L/D)} = 0.33_1$, $P_{(D/L)} = 0.80_8$. The probability of $meso$ arrangement P_m of the DL model is able to be estimated using the following equation:

$$P_m = 1 - 2P_{(L/D)}P_{(D/L)}/(P_{(L/D)} + P_{(D/L)}) \qquad (21)$$

The value of P_m is 0.52_9 and 0.53_1 corresponding to each pair of the values of $P_{(L/D)}$ and $P_{(D/L)}$. These P_m values almost agree with the value of P_m of the mr model (0.53_7). This means that both of the probabilities $P_{(D/D)}$ and $P_{(L/L)}$ calculated on the basis of the mr model are not about 0.53, but one of the probabilities $P_{(D/D)}$ and $P_{(L/L)}$ is about 0.19 and the other is 0.67, because

$$P_{(D/D)} = P_{(AD/D)} + P_{(MD/D)} =$$
$$\begin{cases} 0.18_3 + 0.00_0 = 0.18_3 & \text{(for 1st group)} \\ 0.27_0 + 0.39_9 = 0.66_9 & \text{(for 2nd group)} \end{cases} \qquad (22a)$$

$$P_{(L/L)} = P_{(AL/L)} + P_{(ML/L)} =$$
$$\begin{cases} 0.26_9 + 0.40_0 = 0.66_9 & \text{(for 1st group)} \\ 0.19_4 + 0.00_0 = 0.19_4 & \text{(for 2nd group)} \end{cases} \qquad (22b)$$

Thus, [Bernoulli] − [1st Markov]$_{cor}$ statistics based on DL method give more precise information on polymerization for RMN3 (radical polymerization).

For the sample AMN2, the most suitable statistics is [2nd Markov] − [1st Markov]$_{ind}$ in both the cases of mr and DL models. The four independent parameters, describing the monomer unit sequence ($P_{(A/AA)}$, $P_{(A/AM)}$, $P_{(A/MA)}$, and $P_{(A/MM)}$) for the both models are reasonably very close each other. Regarding the parameters of the 1st order Markov statistics on the cotacticity, the probability parameters $P_{(r/m)}$ and $P_{(m/r)}$ are able to be written as a function of $P_{(D/L)}$ and $P_{(L/D)}$ as follows:

$$P_{(r/m)} = \frac{P_{(D/L)}P_{(L/D)}(2 - P_{(D/L)} - P_{(L/D)})}{P_{(D/L)} + P_{(L/D)} - 2P_{(D/L)}P_{(L/D)}} \qquad (23a)$$

$$P_{(m/r)} = 1 - \frac{P_{(D/L)} + P_{(L/D)}}{2} \qquad (23b)$$

where $P_{(r/m)}$ and $P_{(m/r)}$ express the probabilities of $racemo$ and $meso$ addition to the propagating $meso$ and $racemo$ end, respectively. The eq 23a, b are derived by rearrangement of the following relations[5]:

$$(m) = P_{(m/r)}/(P_{(r/m)} + P_{(m/r)}) \qquad (24a)$$

$$(m) = 1 - 2P_{(L/D)}P_{(D/L)}/(P_{(L/D)} + P_{(D/L)}) \qquad (24b)$$

$$(mm) = (1 - P_{(r/m)})P_{(m/r)}/(P_{(r/m)} + P_{(m/r)}) \qquad (24c)$$

$$(mm) = 1 - P_{(L/D)}P_{(D/L)} - 4P_{(L/D)}P_{(D/L)}/(P_{(L/D)} + P_{(D/L)}) \qquad (24d)$$

Here, (m) and (mm) are diad and triad molar fractions, respectively, consisting of $meso$ sequence only. The substitution of the values of $P_{(D/L)}$ and $P_{(L/D)}$ of the DL model into eq 23a, b gives us $P_{(r/m)} = 0.40_0$ and $P_{(m/r)} = 0.48_9$, both of which are very near to those obtained by the mr model ($P_{(r/m)} = 0.40_0$ and $P_{(m/r)} = 0.48_9$).

For the AN monomers of the sample AMN3, two different values of the probabilities for each case of the $meso$ and $racemo$ arrangements are obtained due to the reflection image relation between D and L form of the monomers. Contrary, the $racemo$ arrangement probability of MAN monomers is zero. Two solutions are obtained only when the MAN monomers add in $meso$ conformation. Interestingly, $P_{(AL/L)}$ is zero when $P_{(AD/D)} = 0.67_9$ and quite conversely $P_{(AD/D)}$ is zero when $P_{(AL/L)} = 0.68_2$, meaning that an AN monomer with L form never adds in $meso$ form when the monomer with D form adds in the same manner or $vice versa$. This situation is quite different from that for RMN3 of which copolymerization statistics also obey [Bernoulli] − [1st Markov]$_{cor}$, in that MAN not AN monomer never adds in DD (or LL) form when LL (or DD) form is realized.

Using eq 20, $P_{(L/D)}$ and $P_{(D/L)}$ of the DL model based on the 1st order Markov statistics are estimated to be $(0.28_0, 0.64_4)$, and $(0.63_8, 0.27_1)$, corresponding to the two values of each probability parameter, such as $P_{(AD/D)}$, $P_{(AL/D)}$, $\cdots$, in the fourth and fifth columns of the Table II. In the same manner as carried out for the sample AMN2, we obtain the parameters $P_{(r/m)}$ and $P_{(m/r)}$ of the 1st order Markov statistics on the mr sequence to be $(0.34_5, 0.53_8)$ and $(0.34_7, 0.54_6)$. The $P_{(r/m)}$ value is very close to that of $P_{(r/m)}$ ($= 0.32_8$) calculated by the mr model. However, the difference of the value of $P_{(m/r)}$ estimated on the basis of the DL and mr model is not negligible. $P_{(m/r)}$ obtained by the DL model seems reliable for this polymer, because, δ'_{min} of the DL model is less than that of the mr model as shown in Table Ic.

The studies up to the present have revealed that the additive reaction of AN,[12−15,17] MAN,[18,19] and vinyl-pyridine[20] in $meso$ conformation will be significantly predominant, if dialkylmagnesium is employed as an initiator, especially at temperatures above 100°C, being in the same temperature region as that used for AMN3 copolymerization. The preferential $meso$ conformation of MAN is explained by the coordination mechanism of six-membered ring formation consisting of a $meso$ diad between ultimate and penultimate monomer units with magnesium. This situation for MAN monomer seems to be preferentially applicable in the copolymerization
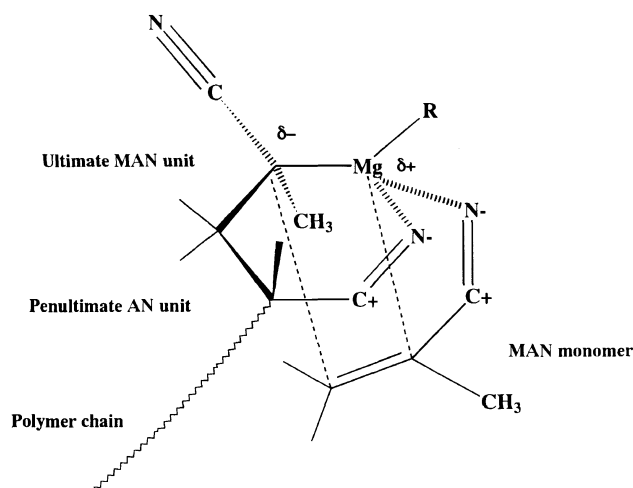
Figure 1. Co-ordination of MAN monomer to a six-membered ring of propagating radical end of poly (AN-co-MAN) using dialkyl-magnesium as an initiator above 100°C in organic solvent.

system of AN and MAN, since $P_{(ML/D)}$ and $P_{(MD/L)}$ are both nearly zero but $P_{(AL/D)}$ and $P_{(AD/L)}$ are 0.27–0.64. Figure 1 shows the structure in which the MAN monomer is regulated strictly and co-ordinates to a six-membered ring of propagating end with *meso* conformation in the copolymerization system.

It is prominently interesting that the sequences of the two different samples, RMN3 prepared radically and AMN3 synthesized anionically high temperature polymerization, obey the same statistical model [Bernoulli] – [1st Markov]$_{cor}$. This agreement, however, may be an accidental one because the methods to prepare them are quite different and the probability parameters in each statistics also differ from the other.

In the case of RMN3 only, the most suitable statistics for *mr*- and *DL*-system are different from each other. The results that Bernoulli and 1st order Markov statistics are suitable for *mr*- and *DL*-type conformational statistics, respectively, means that there exists a mechanism to regulate an addition direction of next monomer in a standpoint of monad, unless there is no effect to do in a standpoint of diad.

MAN monomer in the radical method polymerizes with no significant selectivity, but in the high temperature anionic method it adds almost completely with *meso* conformation. This may be due to the co-ordination structure between MAN monomer and six-membered ring at the propagating end, which causes completely not to add with *racemo* conformation.

The degrees of optimization for the three copolymer samples judging from the values of δ'_{min} can be arrayed in turn as RMN3, AMN2, and AMN3, *i.e.*, 0.83 (0.98), 2.3_1 (2.3_1) and 3.3_7 (4.8_8) for *DL* (*mr*)-type, respectively. As described above, this tendency might depend on the degree of frequency of the side reaction under each copolymerization condition as same as homopolymerization of AN reported previously.[16]

CONCLUSION

1) In a bi-component copolymer system, where each of both monomer units has a possibility of yielding stereoregular homopolymer, equations of copolymer se-

quence distribution were theoretically derived considering chirality sequence distribution strictly based on Markov statistics.

2) *DL* equations newly derived were found to explain well the monomer unit sequence with cotacticity of poly(AN-co-MAN), polymerized both by radical method at 60°C and by anionic methods employing dialkylmagnesium as initiator at temperatures above 100°C, rather than equations based on *mr* style.

3) The reaction probability of high temperature anionic polymerization estimated by [Bernoulli] – [1st Markov]$_{cor}$ statistics has revealed that *racemo* addition of MAN monomer does not occur in the polymerization essentially. This phenomenon seems to be explained by the co-ordination mechanism in the high temperature anionic method reported already by Ono *et al.*[12] and Nakano *et al.*[17] for AN polymerization.

APPENDIX

Appendix A [*Bernoulli*] – [*1st Markov*]$_{cor}$

$$(A^m A^m B) = (P_{(AD/D)}P_{(BD/D)}D^{DL}_{AD} + P_{(AL/L)}P_{(BL/L)}D^{DL}_{AL}$$
$$+ P^2_{(AD/D)}D^{DL}_{BD} + P^2_{(AL/L)}D^{DL}_{BL})/D^{DL(1)} \quad (A.1a)$$

$$(A^m A^r B) = (P_{(AD/D)}P_{(BL/D)}D^{DL}_{AD} + P_{(AL/L)}P_{(BD/L)}D^{DL}_{AL}$$
$$+ P_{(AL/D)}P_{(AL/L)}D^{DL}_{BD}$$
$$+ P_{(AD/D)}P_{(AD/L)}D^{DL}_{BL})/D^{DL(1)} \quad (A.1b)$$

$$(A^r A^m B) = (P_{(AL/D)}P_{(BL/L)}D^{DL}_{AD} + P_{(AD/L)}P_{(BD/D)}D^{DL}_{AL}$$
$$+ P_{(AD/D)}P_{(AL/D)}D^{DL}_{BD}$$
$$+ P_{(AL/L)}P_{(AD/L)}D^{DL}_{BL})/D^{DL(1)} \quad (A.1c)$$

$$(A^r A^r B) = \{P_{(AL/D)}P_{(BD/L)}D^{DL}_{AD}$$
$$+ P_{(AD/L)}P_{(BL/D)}D^{DL}_{AL}$$
$$+ P_{(AL/D)}P_{(AD/L)}(D^{DL}_{BD}$$
$$+ D^{DL}_{BL})\}/D^{DL(1)} \quad (A.1d)$$

$$(B^m A^m B) = (P_{(AD/D)}P_{(BD/D)}D^{DL}_{BD}$$
$$+ P_{(AL/L)}P_{(BL/L)}D^{DL}_{BL})/D^{DL(1)} \quad (A.2a)$$

$$(B^m A^r B) = \{(P_{(AD/D)}P_{(BL/D)}$$
$$+ P_{(AL/D)}P_{(BL/L)})D^{DL}_{BD}$$
$$+ (P_{(AL/L)}P_{(BD/L)}$$
$$+ P_{(AD/L)}P_{(BD/D)})D^{DL}_{BL})/D^{DL(1)} \quad (A.2b)$$

$$(B^r A^r B) = (P_{(AL/D)}P_{(BD/L)}D^{DL}_{BD} + P_{(AD/L)}P_{(BL/D)}D^{DL}_{BL})/D^{DL(1)} \quad (A.2c)$$

$$(A^m B^m A) = (P_{(AD/D)}P_{(BD/D)}D^{DL}_{AD}$$
$$+ P_{(AL/L)}P_{(BL/L)}D^{DL}_{AL})/D^{DL(1)} \quad (A.3a)$$

$$(A^m B^r A) = \{(P_{(AL/D)}P_{(BD/D)} + P_{(AL/L)}P_{(BL/D)})D^{DL}_{AD}$$
$$+ (P_{(AD/L)}P_{(BL/L)}D^{DL}_{AL} + P_{(AD/D)}P_{(BD/L)})\}/D^{DL(1)} \quad (A.3b)$$

$$(A^r B^r A) = (P_{(AD/L)}P_{(BL/D)}D^{DL}_{AD}$$
$$+ P_{(AL/D)}P_{(BD/L)}D^{DL}_{AL})/D^{DL(1)} \quad (A.3c)$$

$$(A^mB^mB) = (P^2_{(BD/D)}D^{DL}_{AD} + P^2_{(BL/L)}D^{DL}_{AL}$$
$$+ P_{(AD/D)}P_{(BD/D)}D^{DL}_{BD}$$
$$+ P_{(AL/L)}P_{(BL/L)}D^{DL}_{BL})/D^{DL(1)} \quad (A.4a)$$

$$(A^mB^rB) = (P_{(BD/D)}P_{(BL/D)}D^{DL}_{AD} + P_{(BD/L)}P_{(BL/L)}D^{DL}_{AL}$$
$$+ P_{(AL/L)}P_{(BL/D)}D^{DL}_{BD}$$
$$+ P_{(AD/D)}P_{(BD/L)}D^{DL}_{BL})/D^{DL(1)} \quad (A.4b)$$

$$(A^rB^mB) = (P_{(BL/D)}P_{(BL/L)}D^{DL}_{AD}$$
$$+ P_{(BD/D)}P_{(BD/L)}D^{DL}_{AL}$$
$$+ P_{(AL/D)}P_{(BD/D)}D^{DL}_{BD}$$
$$+ P_{(AD/L)}P_{(BL/L)}D^{DL}_{BL})/D^{DL(1)} \quad (A.4c)$$

$$(A^rB^rB) = \{P_{(BD/L)}P_{(BL/D)}(D^{DL}_{AD} + D^{DL}_{AL})$$
$$+ P_{(AD/L)}P_{(BL/D)}D^{DL}_{BD}$$
$$+ P_{(AL/D)}P_{(BD/L)}D^{DL}_{BL}\}/D^{DL(1)} \quad (A.4d)$$

$$(B^mB^mB) = (P^2_{(BD/D)}D^{DL}_{BD} + P^2_{(BL/L)}D^{DL}_{BL})/D^{DL(1)} \quad (A.5a)$$

$$(B^mB^rB) = (P_{(BD/D)} + P_{(BL/L)})(P_{(BL/D)}D^{DL}_{BD}$$
$$+ P_{(BD/L)}D^{DL}_{BD})/D^{DL(1)} \quad (A.5b)$$

$$(B^rB^rB) = P_{(BD/L)}P_{(BL/D)}(D^{DL}_{BD} + D^{DL}_{BL})/D^{DL(1)}$$
$$= P_{(BD/L)}P_{(BL/D)}(P_{(B/L)}P_{(L/D)}$$
$$+ P_{(B/D)}P_{(D/L)})/D^{DL(1)} \quad (A.5c)$$

Appendix B $\quad [1st\ Markov] - [Bernoulli]_{cor}$

$$(A^mA^mB) = (P_{(AD/A)}P_{(BD/A)}D^{2M}_{AD} + P_{(AL/A)}P_{(BL/A)}D^{2M}_{AL}$$
$$+ P_{(AD/B)}P_{(AD/A)}D^{2M}_{BD}$$
$$+ P_{(AL/B)}P_{(AL/A)}D^{2M}_{BL})/D^{2M(1)} \quad (A.6a)$$

$$(A^mA^rB) = (P_{(AD/A)}P_{(BL/A)}D^{2M}_{AD} + P_{(AL/A)}P_{(BD/A)}D^{2M}_{AL}$$
$$+ P_{(AL/B)}P_{(AL/A)}D^{2M}_{BD}$$
$$+ P_{(AD/B)}P_{(AD/B)}D^{2M}_{BL})/D^{2M(1)} \quad (A.6b)$$

$$(A^rA^mB) = (P_{(AL/A)}P_{(BL/A)}D^{2M}_{AD} + P_{(AD/A)}P_{(BD/A)}D^{2M}_{AL}$$
$$+ P_{(AD/B)}P_{(AL/A)}D^{2M}_{BD}$$
$$+ P_{(AL/B)}P_{(AD/A)}D^{2M}_{BL})/D^{2M(1)} \quad (A.6c)$$

$$(A^rA^rB) = \{P_{(AL/A)}P_{(BD/A)}D^{2M}_{AD} + P_{(AD/A)}P_{(BL/A)}D^{2M}_{AL}$$
$$+ P_{(AL/B)}P_{(AD/A)}(D^{2M}_{BD} + D^{2M}_{BL})\}/D^{2M(1)} \quad (A.6d)$$

$$(B^mA^mB) = (P_{(AD/B)}P_{(BD/A)}D^{2M}_{BD}$$
$$+ P_{(AL/B)}P_{(BL/A)}D^{2M}_{BL})/D^{2M(1)} \quad (A.7a)$$

$$(B^mA^rB) = P_{(A/B)}(P_{(BL/A)}D^{2M}_{BD} + P_{(BD/A)}D^{2M}_{BL})/D^{2M(1)} \quad (A.7b)$$

$$(B^rA^rB) = (P_{(AL/B)}P_{(BD/A)}D^{2M}_{BD} + P_{(AD/B)}P_{(BL/A)}D^{2M}_{BL})/D^{2M(1)}$$
$$\quad (A.7c)$$

$$(A^mB^mA) = (P_{(AD/B)}P_{(BD/A)}D^{2M}_{AD}$$
$$+ P_{(AL/B)}P_{(BL/A)}D^{2M}_{AL})/D^{2M(1)} \quad (A.8a)$$

$$(A^mB^rA) = P_{(B/A)}(P_{(AL/B)}D^{2M}_{AD} + P_{(AD/B)}D^{2M}_{AL})/D^{2M(1)} \quad (A.8b)$$

$$(A^rB^rA) = (P_{(AD/B)}P_{(BL/A)}D^{2M}_{AD} + P_{(AL/B)}P_{(BD/A)}D^{2M}_{AL})/D^{2M(1)}$$
$$\quad (A.8c)$$

$$(A^mB^mB) = (P_{(BD/A)}P_{(BD/B)}D^{2M}_{AD} + P_{(BL/A)}P_{(BL/B)}D^{2M}_{AL}$$
$$+ P_{(AD/B)}P_{(BD/B)}D^{2M}_{BD}$$
$$+ P_{(AL/B)}P_{(BL/B)}D^{2M}_{BL})/D^{2M(1)} \quad (A.9a)$$

$$(A^mB^rB) = (P_{(BL/A)}P_{(BD/B)}D^{2M}_{AD} + P_{(BL/A)}P_{(BD/B)}D^{2M}_{AL}$$
$$+ P_{(AL/B)}P_{(BL/B)}D^{2M}_{BD}$$
$$+ P_{(AD/B)}P_{(BD/B)}D^{2M}_{BL})/D^{2M(1)} \quad (A.9b)$$

$$(A^rB^mB) = (P_{(BL/A)}P_{(BL/B)}D^{2M}_{AD} + P_{(BD/A)}P_{(BD/B)}D^{2M}_{AL}$$
$$+ P_{(AL/B)}P_{(BD/B)}D^{2M}_{BD}$$
$$+ P_{(AD/B)}P_{(BL/B)}D^{2M}_{BL})/D^{2M(1)} \quad (A.9c)$$

$$(A^rB^rB) = (P_{(BL/A)}P_{(BD/B)}D^{2M}_{AD} + P_{(BD/A)}P_{(BL/B)}D^{2M}_{AL}$$
$$+ P_{(AD/B)}P_{(BL/B)}D^{2M}_{BD}$$
$$+ P_{(AL/B)}P_{(BD/B)}D^{2M}_{BL})/D^{2M(1)} \quad (A.9d)$$

$$(B^mB^mB) = (P^2_{(BD/B)}D^{2M}_{BD} + P^2_{(BL/B)}D^{2M}_{BL})/D^{2M(1)} \quad (A.10a)$$

$$(B^mB^rB) = \{P_{(BL/B)}P_{(BD/B)}(D^{2M}_{BD} + D^{2M}_{BL}) + P^2_{(BL/B)}D^{2M}_{BD}$$
$$+ P^2_{(BD/B)}D^{2M}_{BL}\}/D^{2M(1)} \quad (A.10b)$$

$$(B^rB^rB) = P_{(BD/B)}P_{(BL/B)}(D^{2M}_{BD} + D^{2M}_{BL})/D^{2M(1)} \quad (A.10c)$$

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