

Sequence Distribution of Acrylonitrile/Methacrylonitrile Copolymers

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ABSTRACT: An attempt was made to establish a general theory for the determination of sequence distribution of bi-component copolymers, in which both monomer units each have the possibility of yielding stereoregular homopolymer sequences, assuming that the propagation reaction is explained by probability statistics. Here, the stereoregularity (*i.e.*, cotacticity) of copolymer sequence and its correlations (if any) against copolymer sequence were properly taken into account. The theory was successfully applied to explain the cotacticity of ten acrylonitrile/methacrylonitrile copolymer samples, prepared by radical polymerizations with a redox catalyst, and by anionic polymerizations with organometallic catalyst at lower and higher temperatures. The most adequate statistical models to describe triad sequence distributions, evaluated from ^{13}C NMR spectrum of these polymers, were determined by generalizing Kamide *et al.* method [*Polym. J.*, **17**, 1291 (1985)], used originally for analysis of the stereoregularity of polyacrylonitrile.

KEY WORDS Copolymer Sequence Distribution / Cotacticity / Acrylonitrile/Methacrylonitrile Copolymer / Bernoulli Statistics / Markov Statistics / ^{13}C NMR Spectrometer / Triad Sequence /

When two monomers (*e.g.*, A and B) are independently able to yield stereoregular homopolymers (*e.g.*, AAA \cdots AA and BBB \cdots BB), the cotacticity of copolymer sequences, first introduced by Bovey,¹ is one of the important parameters to characterize A/B copolymers. Table I illustrates copolymer sequences when cotacticity is considered.

Very recently, analysis of copolymer sequence distribution, combined with its cotacticity distribution, was attempted on numerous bi-component copolymers, including methyl acrylate/vinylidene chloride copolymer,² ethylene/propylene copolymer,^{3,4} acrylonitrile/vinylidene chloride copolymer,^{5,6} styrene/methyl methacrylate copolymer,⁷ methacrylonitrile/ α -methylstyrene copolymer,⁸ methyl methacrylate/methacrylic acid copolymer,⁹ acrylonitrile/methyl methacrylate copolymer,^{10,11} acrylonitrile/ethyl methacrylate copolymer,¹² acrylonitrile/styrene copolymer,¹³ vinyl acetate/vinyl

alcohol copolymer,¹⁴ and methyl acrylate/ethyl acrylate copolymer.¹⁵

Almost all of these studies are based on a model which includes cotacticity parameters σ_{AA} , σ_{AB} , σ_{BA} , and σ_{BB} proposed by Bovey.¹⁶ Expression of all 20 triads in this model is given by Klesper and Sielaff.¹⁷ But applicability of this model (hereafter referred to as σ -parameter model) is severely restricted to very particular cases: 1st order Markov process for compositional sequence and Bernoulli process for its cotacticity (they are simply represented as [1st order Markov]—[Bernoulli], respectively) and it cannot be extended simply for studies on higher compositional statistics than 1st order Markov or that on higher configurational statistics than the Bernoulli process. General copolymers do not always obey the σ -parameter model.

In this article, a general theory for lower conversion and azeotropic polymerization

Table I. Cotacticity of copolymer consisting mono- and disubstituted monomers

		Copolymer containing two mono-substituted monomers	Copolymer containing two di substituted monomers
Monomer	A	$\text{CH}_2=\text{CHX}$	$\text{CH}_2=\text{CXx}$
	B	$\text{CH}_2=\text{CHY}$	$\text{CH}_2=\text{CYy}$
Structure of the molecular chain			
Copolymer sequence considered cotacticity		A ^r A ^r B ^m A ^r B ^m B	A ^r A ^r B ^m A ^r B ^m B

samples is presented to describe all diad and triad copolymer sequence distributions in terms of some probability statistics including Bernoulli, 1st and 2nd order Markov processes.

Note that monomer unit sequence distribution [*e.g.*, AABABB in Table I] and its cotacticity distribution (*i.e.*, distribution of cotacticity of the monomer unit sequence) [*e.g.*, *rrmm* in Table I] may or may not obey the same statistical model, and also monomer unit sequence distribution does or does not correlate with cotacticity distribution. Hereafter, we refer to the former case as "correlation" and to the latter as "non-correlation." In other words, the diad cotacticity of growing chain end and its adjacent monomer unit does or does not influence the kind of monomer unit to be added at the end, and the monomer unit sequence does or does not effect diad cotacticity formed by the chain end and newly added monomer unit.

In order to illustrate the applicability of the theory presented here, ten acrylonitrile (AN)/methacrylonitrile (MAN) copolymer samples were synthesized. Tacticities of polyacrylonitrile¹⁸ and polymethacrylonitrile^{19,20} (homopolymers of AN and MAN, hereafter referred to as PAN and PMAN, respectively) are well-known to be controlled over a wide range by choosing adequate preparative conditions. The most reasonable combination of statistical

models for each samples was determined by generalizing the method ("an alternative method") of Kamide *et al.*²¹ originally utilized for analysis on tacticity of PAN.

The theory presented in this article is not restricted to the AN/MAN copolymer only, but also able to applies to general copolymer systems. We are preparing reports of studies on other copolymer cases shown in the literature 6, 11, and 12.

THEORETICAL BACKGROUND

In this study, copolymer sequence means monomer unit sequence, in which cotacticity is considered concurrently. Mole fractions of diad sequence such as A^mA and A^rB are expressed by adding parenthesis marks at both ends of a sequence notation, for example, as (A^mA) and (A^rB). Here, *m* and *r* mean comeso and coracemo configurations, respectively. Expression giving the mole fractions from various probabilities is shown below and in Appendix.

(A) Non-Correlation Case

The subcase A1 where both monomer unit sequence distribution and its cotacticity distribution obey Bernoulli statistics (hereafter referred to as [Bernoulli]–[Bernoulli](non-correlation)):

If P_A is referred to as the probability for the addition of monomer unit A to growing chain end, $P_B (\equiv 1 - P_A)$, the probability for addition of monomer unit B, P_m , the probability of meso arrangement, $P_r (\equiv 1 - P_m)$, the probability of racemo arrangement, the mole fractions of diad copolymer sequences of all the types (in this case, 6) are given by,⁶

$$(A^m A) = P_A^2 P_m \quad (1a)$$

$$(A^r A) = P_A^2 P_r \quad (1b)$$

$$(A^m B) = 2P_A P_B P_m \quad (1c)$$

$$(A^r B) = 2P_A P_B P_r \quad (1d)$$

$$(B^m B) = P_B^2 P_m \quad (1e)$$

$$(B^r B) = P_B^2 P_r \quad (1f)$$

In case where the fractions of the above diad sequences are determined experimentally from NMR spectrum, P_A and P_m can be evaluated from eq 1a—1f. The mole fractions of 20 triad sequences are also expressed in a similar manner.

Other non-correlation subcases are described in the same manner as multiplication of the monomer unit sequence part by the cotacticity part.

(B) Correlation Case

The subcase B1 where both monomer unit sequence distribution and its cotacticity distribution obey Bernoulli statistics ([Bernoulli]–[Bernoulli](correlation)):

If P_{mA} is referred to as the probability for formation of meso arrangement by addition of monomer unit A, P_{rA} , the probability for

addition of monomer unit A to the growing chain end, and other notations have similar meanings, the mole fractions of diad copolymer sequences are expressed as:

$$(A^m A) = P_A P_{mA} \quad (2a)$$

$$(A^r A) = P_A P_{rA} \quad (2b)$$

$$(A^m B) = P_A P_{mB} + P_B P_{mA} \quad (2c)$$

$$(A^r B) = P_A P_{rB} + P_B P_{rA} \quad (2d)$$

$$(B^m B) = P_B P_{mB} \quad (2e)$$

$$(B^r B) = P_B P_{rB} \quad (2f)$$

The mole fractions of 20 triad sequences are also described similarly. Note that the following equations hold,

$$P_A = P_{mA} + P_{rA} \quad (3a)$$

$$P_B = P_{mB} + P_{rB} \quad (3b)$$

$$P_{mA} + P_{rA} + P_{mB} + P_{rB} = 1 \quad (3c)$$

The subcase B2 where monomer unit sequence distribution obeys Bernoulli statistics and its cotacticity distribution obeys 1st order Markov statistics ([Bernoulli]–[1st order Markov](correlation)):

If $P_{(m/r)}$ is referred to as the probability for the addition of meso arrangement to the growing chain ending in racemo arrangement, $P_{(rA/m)}$, the probability for addition of monomer A to the growing chain ending in meso arrangement with formation of a racemo arrangement, and other parameters have analogous meaning, and $(P_{(r/m)} + P_{(m/r)})^2$ is shortly referred to as X , the mole fractions of 6 diads are described as follows,

$$(A^m A) = (P_{(m/r)} P_{(A/m)} + P_{(r/m)} P_{(A/r)}) (P_{(m/r)} P_{(mA/m)} + P_{(r/m)} P_{(mA/r)}) / X \quad (4a)$$

$$(A^r A) = (P_{(m/r)} P_{(A/m)} + P_{(r/m)} P_{(A/r)}) (P_{(m/r)} P_{(rA/m)} + P_{(r/m)} P_{(rA/r)}) / X \quad (4b)$$

$$(A^m B) = \{ (P_{(m/r)} P_{(A/m)} + P_{(r/m)} P_{(A/r)}) (P_{(m/r)} P_{(mB/m)} + P_{(r/m)} P_{(mB/r)}) + (P_{(m/r)} P_{(B/m)} + P_{(r/m)} P_{(B/r)}) (P_{(m/r)} P_{(mA/m)} + P_{(r/m)} P_{(mA/r)}) \} / X \quad (4c)$$

$$(A^r B) = \{ (P_{(m/r)} P_{(A/m)} + P_{(r/m)} P_{(A/r)}) (P_{(m/r)} P_{(rB/m)} + P_{(r/m)} P_{(rB/r)}) + (P_{(m/r)} P_{(B/m)} + P_{(r/m)} P_{(B/r)}) (P_{(m/r)} P_{(rA/m)} + P_{(r/m)} P_{(rA/r)}) \} / X \quad (4d)$$

$$(B^mB) = (P_{(m/r)}P_{(B/m)} + P_{(r/m)}P_{(B/r)})(P_{(m/r)}P_{(mB/m)} + P_{(r/m)}P_{(mB/r)})/X \quad (4e)$$

$$(B^rB) = (P_{(m/r)}P_{(B/m)} + P_{(r/m)}P_{(B/r)})(P_{(m/r)}P_{(rB/m)} + P_{(r/m)}P_{(rB/r)})/X. \quad (4f)$$

In this case $P_{(m/m)} = P_{(mA/m)} + P_{(mB/m)}$, $P_{(r/m)} = P_{(rA/m)} + P_{(rB/m)}$, $P_{(m/r)} = P_{(mA/r)} + P_{(mB/r)}$ and $P_{(r/r)} = P_{(rA/r)} + P_{(rB/r)}$ hold. Also $P_{(A/m)} = P_{(mA/m)} + P_{(rA/m)}$, $P_{(A/r)} = P_{(mA/r)} + P_{(rA/r)}$, $P_{(B/m)} = P_{(mB/m)} + P_{(rB/m)}$ and $P_{(B/r)} = P_{(mB/r)} + P_{(rB/r)}$ hold.

The mole fractions of 20 triad copolymer sequences are:

$$(A^m A^m A) = (P_{(m/r)}P_{(A/m)} + P_{(r/m)}P_{(A/r)})(P_{(m/r)}P_{(mA/m)} + P_{(r/m)}P_{(mA/r)})P_{(mA/m)}/X \quad (5a)$$

$$(A^m A^r A) = (P_{(m/r)}P_{(A/m)} + P_{(r/m)}P_{(A/r)})\{(P_{(m/r)}P_{(mA/m)} + P_{(r/m)}P_{(mA/r)})P_{(rA/m)} + (P_{(m/r)}P_{(rA/m)} + P_{(r/m)}P_{(rA/r)})P_{(mA/r)}\}/X \quad (5b)$$

$$(A^r A^r A) = (P_{(m/r)}P_{(A/m)} + P_{(r/m)}P_{(A/r)})(P_{(m/r)}P_{(rA/m)} + P_{(r/m)}P_{(rA/r)})P_{(rA/r)}/X \quad (5c)$$

$$(A^m A^m B) = (P_{(m/r)}P_{(mA/m)} + P_{(r/m)}P_{(mA/r)})\{(P_{(m/r)}P_{(A/m)} + P_{(r/m)}P_{(A/r)})P_{(mB/m)} + (P_{(m/r)}P_{(B/m)} + P_{(r/m)}P_{(B/r)})P_{(mA/m)}\}/X \quad (6a)$$

$$(A^m A^r B) = \{(P_{(m/r)}P_{(A/m)} + P_{(r/m)}P_{(A/r)})(P_{(m/r)}P_{(mA/m)} + P_{(r/m)}P_{(mA/r)})P_{(rB/m)} + (P_{(m/r)}P_{(B/m)} + P_{(r/m)}P_{(B/r)})(P_{(m/r)}P_{(rA/m)} + P_{(r/m)}P_{(rA/r)})P_{(mA/r)}\}/X \quad (6b)$$

$$(A^r A^m B) = \{(P_{(m/r)}P_{(A/m)} + P_{(r/m)}P_{(A/r)})(P_{(m/r)}P_{(rA/m)} + P_{(r/m)}P_{(rA/r)})P_{(mB/m)} + (P_{(m/r)}P_{(B/m)} + P_{(r/m)}P_{(B/r)})(P_{(m/r)}P_{(mA/m)} + P_{(r/m)}P_{(mA/r)})P_{(rA/m)}\}/X \quad (6c)$$

$$(A^r A^r B) = (P_{(m/r)}P_{(rA/m)} + P_{(r/m)}P_{(rA/r)})\{(P_{(m/r)}P_{(A/m)} + P_{(r/m)}P_{(A/r)})P_{(rB/r)} + (P_{(m/r)}P_{(B/m)} + P_{(r/m)}P_{(B/r)})P_{(rA/r)}\}/X \quad (6d)$$

$$(B^m A^m B) = (P_{(m/r)}P_{(B/m)} + P_{(r/m)}P_{(B/r)})(P_{(m/r)}P_{(mA/m)} + P_{(r/m)}P_{(mA/r)})P_{(mB/m)}/X \quad (7a)$$

$$(B^m A^r B) = (P_{(m/r)}P_{(B/m)} + P_{(r/m)}P_{(B/r)})\{(P_{(m/r)}P_{(mA/m)} + P_{(r/m)}P_{(mA/r)})P_{(rB/m)} + (P_{(m/r)}P_{(rA/m)} + P_{(r/m)}P_{(rA/r)})P_{(mB/r)}\}/X \quad (7b)$$

$$(B^r A^r B) = (P_{(m/r)}P_{(B/m)} + P_{(r/m)}P_{(B/r)})(P_{(m/r)}P_{(rA/m)} + P_{(r/m)}P_{(rA/r)})P_{(rB/r)}/X \quad (7c)$$

$$(A^m B^m A) = (P_{(m/r)}P_{(A/m)} + P_{(r/m)}P_{(A/r)})(P_{(m/r)}P_{(mB/m)} + P_{(r/m)}P_{(mB/r)})P_{(mA/m)}/X \quad (8a)$$

$$(A^m B^r A) = (P_{(m/r)}P_{(A/m)} + P_{(r/m)}P_{(A/r)})\{(P_{(m/r)}P_{(mB/m)} + P_{(r/m)}P_{(mB/r)})P_{(rA/m)} + (P_{(m/r)}P_{(rB/m)} + P_{(r/m)}P_{(rB/r)})P_{(mA/r)}\}/X \quad (8b)$$

$$(A^r B^r A) = (P_{(m/r)}P_{(A/m)} + P_{(r/m)}P_{(A/r)})(P_{(m/r)}P_{(rB/m)} + P_{(r/m)}P_{(rB/r)})P_{(rA/r)}/X \quad (8c)$$

$$(A^m B^m B) = (P_{(m/r)}P_{(mB/m)} + P_{(r/m)}P_{(mB/r)})\{(P_{(m/r)}P_{(A/m)} + P_{(r/m)}P_{(A/r)})P_{(mB/m)} + (P_{(m/r)}P_{(B/m)} + P_{(r/m)}P_{(B/r)})P_{(mA/m)}\}/X \quad (9a)$$

$$(A^m B^r B) = \{(P_{(m/r)}P_{(A/m)} + P_{(r/m)}P_{(A/r)})(P_{(m/r)}P_{(mB/m)} + P_{(r/m)}P_{(mB/r)})P_{(rB/m)} + (P_{(m/r)}P_{(B/m)} + P_{(r/m)}P_{(B/r)})(P_{(m/r)}P_{(rB/m)} + P_{(r/m)}P_{(rB/r)})P_{(mA/r)}\}/X \quad (9b)$$

$$(A^r B^m B) = \{(P_{(m/r)}P_{(A/m)} + P_{(r/m)}P_{(A/r)})(P_{(m/r)}P_{(rB/m)} + P_{(r/m)}P_{(rB/r)})P_{(mB/r)} + (P_{(m/r)}P_{(B/m)} + P_{(r/m)}P_{(B/r)})(P_{(m/r)}P_{(mB/m)} + P_{(r/m)}P_{(mB/r)})P_{(rA/m)}\}/X \quad (9c)$$

$$(A^r B^r B) = (P_{(m/r)}P_{(rB/m)} + P_{(r/m)}P_{(rB/r)})\{(P_{(m/r)}P_{(A/m)} + P_{(r/m)}P_{(A/r)})P_{(rB/r)}\}$$

$$+ (P_{(m/r)}P_{(B/m)} + P_{(r/m)}P_{(B/r)})P_{(rA/r)}\} / X \quad (9d)$$

$$(B^m B^m B) = (P_{(m/r)}P_{(B/m)} + P_{(r/m)}P_{(B/r)})(P_{(m/r)}P_{(mB/m)} + P_{(r/m)}P_{(mB/r)})P_{(mB/m)} / X \quad (10a)$$

$$(B^m B^r B) = (P_{(m/r)}P_{(B/m)} + P_{(r/m)}P_{(B/r)})\{ (P_{(m/r)}P_{(mB/m)} + P_{(r/m)}P_{(mB/r)})P_{(rB/m)} + (P_{(m/r)}P_{(rB/m)} + P_{(r/m)}P_{(rB/r)})P_{(mB/r)}\} / X \quad (10b)$$

$$(B^r B^r B) = (P_{(m/r)}P_{(B/m)} + P_{(r/m)}P_{(B/r)})(P_{(m/r)}P_{(rB/m)} + P_{(r/m)}P_{(rB/r)})P_{(rB/r)} / X. \quad (10c)$$

In the same manner, all diad and triad copolymer sequence distributions can be expressed by statistical probabilities in cases where monomer unit distribution obeys Bernoulli, 1st or 2nd order Markov statistics and cotacticity distribution obeys Bernoulli, 1st and 2nd order Markov statistics. We derived expressions for models containing less than nine independent parameters. The Appendix includes the results for the case of [1st order Markov]–[Bernoulli](non-correlation) and [Bernoulli]–[1st order Markov](correlation).

Table II compiles parameters for given combination of one statistics chosen among these three statistics for monomer unit sequence distribution, and one statistics among three statistics for cotacticity distribution. In the table the number is total number of parameters and the number in parenthesis means the number of independent variables. Except for [1st order Markov]–[2nd order Markov](correlation), [2nd Markov]–[1st (and 2nd) order Markov](correlation), all parameters can be determined unambiguously and the mole fractions of all diad or triad copolymer sequences can be estimated by an adequate method.

Triad monomer sequence (*i.e.*, AAA, AAB, BAB, ABA, ABB, and BBB) can be evaluated from following equations,

$$(AAA) = (A^m A^m A) + (A^m A^r A) + (A^r A^r A) \quad (11a)$$

$$(AAB) = (A^m A^m B) + (A^m A^r B) + (A^r A^m B) + (A^r A^r B) \quad (11b)$$

$$(BAB) = (B^m A^m B) + (B^m A^r B) \quad (11c)$$

$$+ (B^r A^r B) \quad (11c)$$

$$(ABA) = (A^m B^m A) + (A^m B^r A) + (A^r B^r A) \quad (11d)$$

$$(ABB) = (A^m B^m B) + (A^m B^r B) + (A^r B^m B) + (A^r B^r B) \quad (11e)$$

$$(BBB) = (B^m B^m B) + (B^m B^r B) + (B^r B^r B). \quad (11f)$$

Here $(A^m A^m A)$, $(A^m A^r A)$, \dots , $(B^m B^r B)$ and $(B^r B^r B)$ can be determined from statistical probabilities through use of eq 5a–10c, eq A.1a–A.6c, eq A.8a–A.13c.

Triad tacticity or cotacticity (*i.e.*, (co)isotactic *mm*, (co)heterotactic *mr*, and (co)syndiotactic *rr*) can be evaluated through use of the relations,

$$(mm)_C = (A^m A^m A) + (A^m A^m B) + (A^m B^m B) + (B^m A^m B) + (A^m B^m A) + (B^m B^m B) \quad (12a)$$

$$(mm)_A = (A^m A^m A) \quad (12b)$$

$$(mm)_B = (B^m B^m B) \quad (12c)$$

$$(mr)_C = (A^m A^r A) + (A^m A^r B) + (A^m B^r B) + (B^m A^r B) + (A^m B^r A) + (B^m B^r B) \quad (12d)$$

$$(mr)_A = (A^m A^r A) \quad (12e)$$

$$(mr)_B = (B^m B^r B) \quad (12f)$$

$$(rr)_C = (A^r A^r A) + (A^r A^r B) + (A^r B^r B) + (B^r A^r B) + (A^r B^r A) + (B^r B^r B) \quad (12g)$$

$$(rr)_A = (A^r A^r A) \quad (12h)$$

$$(rr)_B = (B^r B^r B). \quad (12i)$$

Table II. Statistical probability generating monomer unit sequence and cotacticity

Monomer unit sequence	Cotacticity					
	Bernoulli		1st-order Markov		2nd-order Markov	
	Non-correlation	Correlation	Non-correlation	Correlation	Non-correlation	Correlation
Bernoulli	P_m, P_r P_A, P_B	P_{mA}, P_{rA} P_{mB}, P_{rB}	$P_{(m/m)}, P_{(r/m)}$ $P_{(m/r)}, P_{(r/r)}$ P_A, P_B	$P_{(mA/m)}, P_{(rA/m)}$ $P_{(mB/m)}, P_{(rB/m)}$ $P_{(mA/r)}, P_{(rA/r)}$ $P_{(mB/r)}, P_{(rB/r)}$	$P_{(m/mm)}, P_{(r/mm)}$ $P_{(m/mr)}, P_{(r/mr)}$ $P_{(m/rm)}, P_{(r/rm)}$ $P_{(m/r r)}, P_{(r/r r)}$ P_A, P_B	Not calculated
	4 ^a (2) ^b	4 (3)	6 (3)	8 (6)	10 (5)	
1st-order Markov	P_m, P_r $P_{(A/A)}, P_{(B/A)}$ $P_{(A/B)}, P_{(B/B)}$	$P_{(mA/A)}, P_{(rA/A)}$ $P_{(mB/A)}, P_{(rB/A)}$ $P_{(mA/B)}, P_{(rA/B)}$ $P_{(mB/B)}, P_{(rB/B)}$	$P_{(m/m)}, P_{(r/m)}$ $P_{(m/r)}, P_{(r/r)}$ $P_{(A/A)}, P_{(B/A)}$ $P_{(A/B)}, P_{(B/B)}$	Not calculated	$P_{(m/mm)}, P_{(r/mm)}$ $P_{(m/mr)}, P_{(r/mr)}$ $P_{(m/rm)}, P_{(r/rm)}$ $P_{(m/r r)}, P_{(r/r r)}$ $P_{(A/A)}, P_{(B/A)}$ $P_{(A/B)}, P_{(B/B)}$	Not calculated
	6 (3)	8 (6)	8 (4)		12 (6)	
2nd-order Markov	P_m, P_r $P_{(A/AA)}, P_{(B/AA)}$ $P_{(A/AB)}, P_{(B/AB)}$ $P_{(A/BA)}, P_{(B/BA)}$ $P_{(A/BB)}, P_{(B/BB)}$	Not calculated	$P_{(m/m)}, P_{(r/m)}$ $P_{(m/r)}, P_{(r/r)}$ $P_{(A/AA)}, P_{(B/AA)}$ $P_{(A/AB)}, P_{(B/AB)}$ $P_{(A/BA)}, P_{(B/BA)}$ $P_{(A/BB)}, P_{(B/BB)}$	Not calculated	$P_{(m/mm)}, P_{(r/mm)}$ $P_{(m/mr)}, P_{(r/mr)}$ $P_{(m/rm)}, P_{(r/rm)}$ $P_{(m/r r)}, P_{(r/r r)}$ $P_{(A/AA)}, P_{(B/AA)}$ $P_{(A/AB)}, P_{(B/AB)}$ $P_{(A/BA)}, P_{(B/BA)}$ $P_{(A/BB)}, P_{(B/BB)}$	Not calculated
	10 (5)		12 (6)		16 (8)	

^a Total number of parameters in a given statistical model.

^b Number of independent parameters.

Here, the suffix C means cotacticity, and suffixes A and B, all A triads and all B triads, respectively.

If L_A and L_B are referred to as the number-average lengths of sequences consisting of the same monomer units of A and B, respectively, they are evaluated from the following relations,²²

$$L_A = (A) / \{(AB)/2\} \\ = \{(AAA) + (AAB) + (BAB)\} \\ / \{(BAB) + (AAB)/2\} \quad (13a)$$

$$L_B = (B) / \{(AB)/2\} \\ = \{(ABA) + (ABB) + (BBB)\} \\ / \{(ABA) + (ABB)/2\} . \quad (13b)$$

Similarly, if L_m and L_r are referred to as the number-average lengths of sequences consisting of the same configuration of comeso and coracemo, respectively, they are evaluated from the following equations,²³

$$L_m = (m) / \{(mr)/2\} = \{2(mm) + (mr)\} / (mr) \quad (14a)$$

$$L_r = (r) / \{(mr)/2\} = \{2(rr) + (mr)\} / (mr) . \quad (14b)$$

The statistical parameters above are experimentally evaluated directly from the experimental ¹³C NMR data in an ideal case when the peaks corresponding to all the sequences are located each other. The consistency of a given statistical model can be examined using

experimentally evaluated mole fractions of all possible copolymer diad or triad sequences.

However, many actual cases are not ideal: the limited number of mole fractions can only be evaluated experimentally. Often a single peak is attributed to two or three sequences. In this case, we introduce a parameter δ' defined by the relation⁶:

$$\delta' = \sqrt{\sum_{i=1}^N (X_i - Y_i)^2 / N} \quad (15)$$

where X_i and Y_i are the experimental and calculated fractions for a specific diad or triad sequence, respectively, and N is the total number of triad sequences ($N=6$ for diad sequence, $N=20$ for triad sequence). If some peaks of ¹³C NMR data are attributed to plural sequences, X_i and Y_i should be taken as the sum of them and N should be reduced. Y_i can be calculated by utilizing the assumed values of all parameters in eq 1a–10c. We can determine the most probable set of the parameters (*e.g.*, P_A , P_B , P_m , and P_r in A1 subcase) so as to minimize δ' (hereafter referred to as δ'_{\min}). The most reasonable combination of statistics can be chosen among those by judging the magnitude of δ'_{\min} .

EXPERIMENTAL

Preparation of Polymer Samples

A reagent grade AN manufactured by Tokyo Kasei Kogyo Co., Ltd., Tokyo and a special grade MAN manufactured by Wako Pure Chemical Industries, Ltd., Osaka, Japan were purified by distillation with calcium hydride.

Sample code RMN3 was prepared by radically polymerizing a mixture of AN and MAN (molar ratio 56/44) in water for 1 h at 60°C with ammonium persulfate and sodium bisulfite as catalyst. Under these conditions atactic homopolymers (PAN and PMAN) are obtained from AN²⁴ and MAN²⁵, respectively.

Sample codes AMN2, AMN7, and AMN8 were prepared by the anionic polymerization of AN/MAN mixture in toluene at –77°C with *n*-butylethylmagnesium (commercially available as *n*-heptane solution from Tosoh Akzo Corporation, Tokyo) as catalyst.

Sample codes AMN3, AMN9, AMN10, AMN11, AMN12, and AMN13 were prepared by anionic polymerization in mixed xylene using the same catalyst at –77°C. It is known that anionic polymerization gives PAN or PMAN relatively low isotacticity²⁶ at low

Table III. Polymerization conditions of acrylonitrile (A)/methacrylonitrile (M) copolymers and results

Sample code	Polymerization condition					Polymerization result	
	Polymerization (radical or anionic)	Catalyst	Monomer feed ratio	Solvent	Temperature	Copolymer composition	Conversion
			A/M (mol/mol)		°C		
RMN3	Radical	APS–SBS ^a	56/44	Water	60	0.444/0.556	5.5
AMN2	Anionic	BEM ^b	10/90	Toluene	–77	0.837/0.163	7.8
AMN7	Anionic	BEM	3/97	Toluene	–77	0.584/0.416	6.2
AMN8	Anionic	BEM	3/98	Toluene	–77	0.091/0.909	5.6
AMN13	Anionic	BEM	30/70	Mixed xylene	120	0.922/0.078	6.2
AMN3	Anionic	BEM	20/80	Mixed xylene	120	0.841/0.159	4.1
AMN11	Anionic	BEM	10/90	Mixed xylene	120	0.699/0.301	4.7
AMN9	Anionic	BEM	5/95	Mixed xylene	120	0.483/0.517	3.3
AMN10	Anionic	BEM	4/96	Mixed xylene	120	0.279/0.721	2.7
AMN12	Anionic	BEM	2/98	Mixed xylene	120	0.198/0.802	2.5

^a APS, (NH₄)₂S₂O₈; SBS, NaHSO₃.

^b BEM, *n*-butylethylmagnesium.

temperature and yields isotactic PAN¹⁸ or PMAN^{19,20} at high temperature. Table III compiles detailed preparative conditions of these ten AN/MAN copolymer samples. The polymers prepared thus were used without fractionation for further study.

¹³C NMR Measurement

¹³C NMR measurements on the AN/MAN copolymer samples were made on a FT-NMR spectrometer (JEOL GSX-400) using deuterated dimethyl sulfoxide (DMSO)-*d*₆ as the solvent under operating conditions as follows: complete decouple mode, polymer concentration 5 wt%, pulse width 12.0 μs (90° pulse), number of pulse over than 4000, data point 32 K, temperature 80°C, internal standard tetramethylsilane.

RESULTS AND DISCUSSION

Figure 1 shows ¹³C NMR spectra for the CN carbon region of ten AN/MAN copolymer samples. Figure 2 shows typical spectrum of RMN3, and the number is given from the higher magnetic peak.

According to the method of Kamide *et al.*²⁴ for determination of peak assignments of PAN, chemical shifts of peaks in CN carbon region of ¹³C NMR spectrum for AN/MAN copolymer in DMSO-*d*₆ were deductively assigned. In addition to the parameter δ of diminishing shielding effect due to CN triple bond and parameter σ_1 of deshielding effect of the electron density diminishing on a CN carbon due to double bond nature of CN in an *m* arrangement, we define the third parameter η as the shift effect of CN carbon to lower magnetic field caused by the substitution of methine hydrogen in adjacent monomer unit with methyl group.

Using again the following assumptions (1)–(4) originally employed by Kamide *et al.*¹⁹ for PAN:

(1) The coracemo *r* part of AN-centered triad sequence of AM/MAN copolymer is

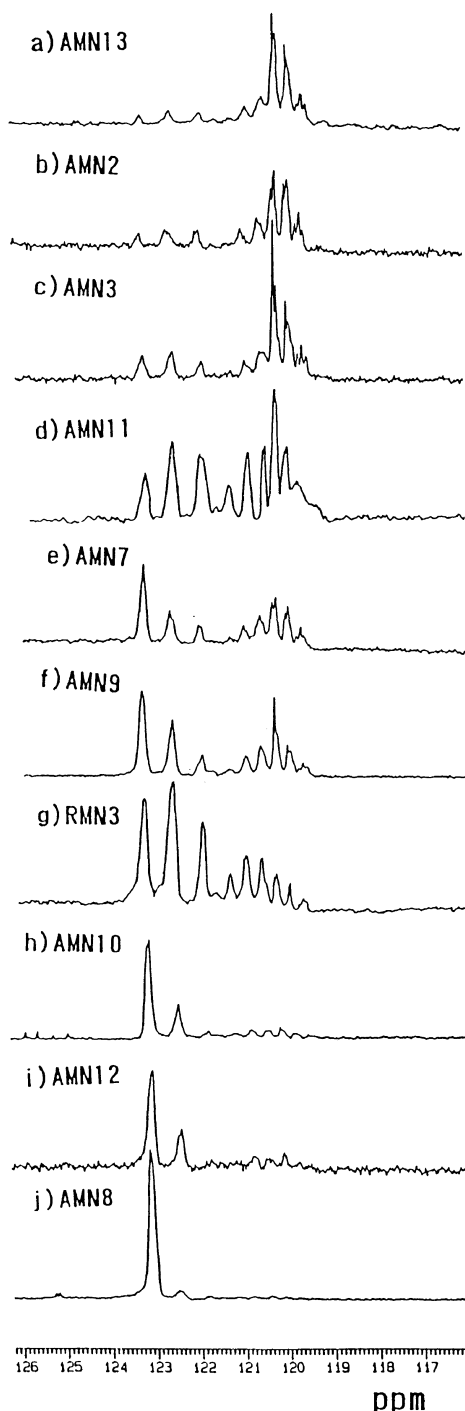


Figure 1. ¹³C NMR spectra for the CN carbon region of acrylonitrile/methacrylonitrile copolymer: a), AMN13; b), AMN2; c), AMN3; d), AMN11; e), AMN7; f), AMN9; g), RMN3; h), AMN10; i), AMN12; j), AMN8.

Sequence Distribution of AN/MAN Copolymer

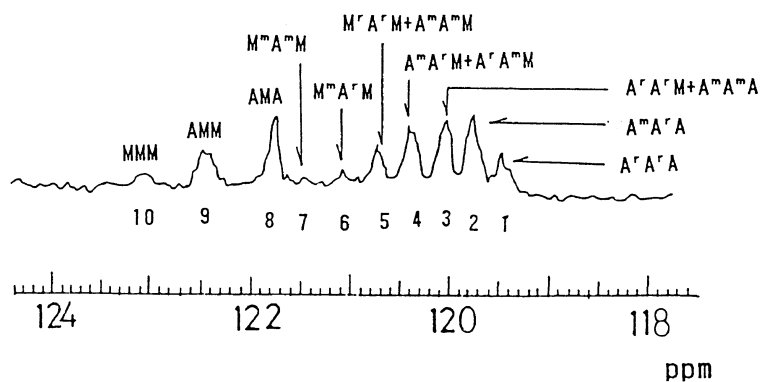


Figure 2. ^{13}C NMR peak assignment in CN region of acrylonitrile (A)/methacrylonitrile (M) copolymer.

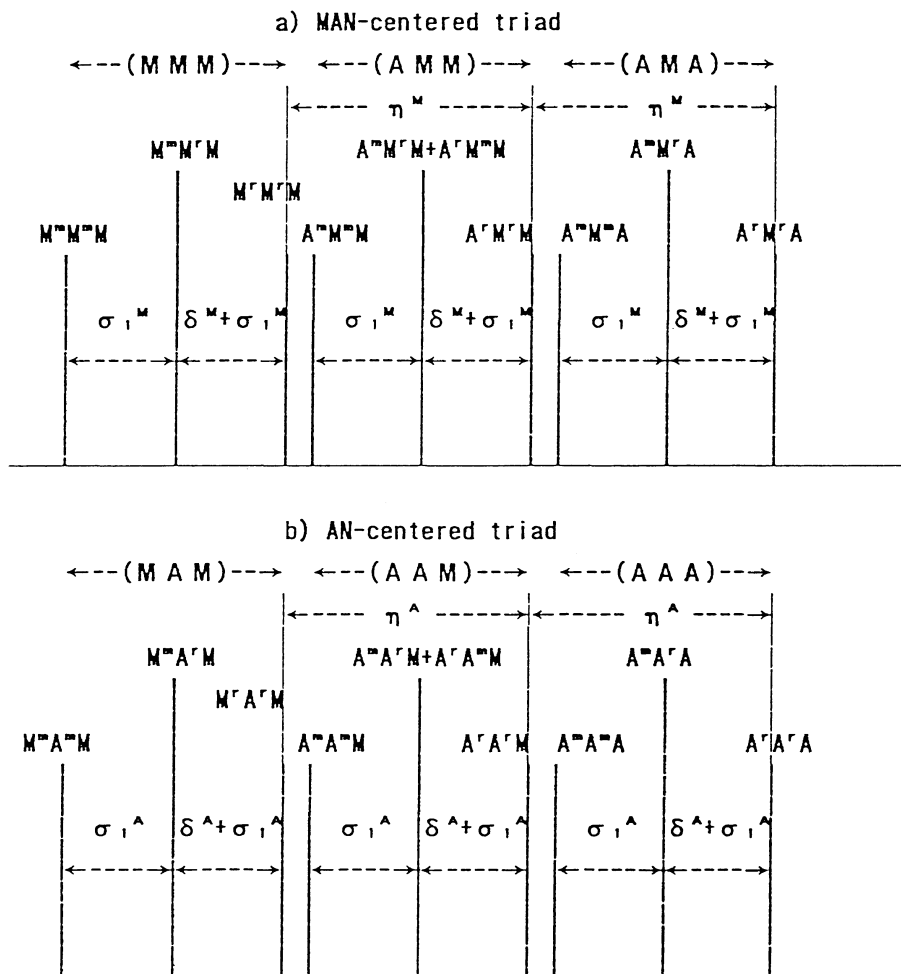


Figure 3. Schematic representation of relative chemical shifts in the CN carbon region of acrylonitrile (A)/methacrylonitrile (M) copolymer using chemical shift parameters: a), MAN-centered triad; b), AN-centered triad.

energetically stable in a *trans-trans* conformation.

(2) The comeso *m* part of AN centered triad sequence of AM/MAN copolymer takes a *trans-trans* or almost *trans-trans* conformation, in which adjacent CN groups in *m* arrangement have a double bond nature as a result of interaction with each other.

(1',2') The coracemo and comeso part of MAN-centered triad sequence of AN/MAN copolymer takes a *trans-trans* or almost *trans-trans* conformation.

(3) Interaction with adjacent CN groups is stable even in solution.

(4) Intermolecular interaction of AN/MAN copolymer is negligibly small.

We can qualitatively estimate the NMR peak position of a given carbon atom of CN in a monomer unit, relative to that for the CN carbon positioned at the center of each *rr* triad sequence consisting of the same monomer units. Based on these assumptions and using

chemical shift parameters, δ , σ_1 , and η introduced above, the relative chemical shifts of 20 triad sequences are described in Table IVa.

Figure 3 is schematic representation of these relative chemical shifts. The upper suffixes A and M mean AN- and MAN-centered triads, respectively. The peaks due to $A^m A^m A$, $A^m A^r A$, and $A^r A^r A$ triad sequences of homopolyacrylonitrile appear at 120.0–1, 119.7–8, and 119.4–5 ppm, respectively,²² and this information gives estimation of δ^A and σ_1^A as 0.04 and 0.30, respectively. The peaks of $M^m M^m M$, $M^m M^r M$, and $M^r M^r M$ triad sequences of homopolymethacrylonitrile correspond to a single peak at 123.1 ppm.¹⁹ From these data, we conclude δ^M and σ_1^M to be almost zero.

Using these values of δ^A , σ_1^A , δ^M , and σ_1^M , we can rewrite the relative chemical shifts in Table IVb. Twenty peaks due to 20 triad sequences are reduced to 12, but only 10 peaks are observed in CN region of ¹³C NMR spectra for AN/MAN copolymers. In order to reduce two more peaks, $\eta^A = 0.64$ or $\eta^M = 0$ is required. From systematic variation of the intensity of

Table IVa. Relative chemical shifts for ¹³C NMR peaks in CN carbon region of acrylonitrile (A)/methacrylonitrile (M) copolymer

Triad sequence	Relative chemical shift/ppm	Triad sequence	Relative chemical shift/ppm
A ^r A ^r A	0	A ^m M ^r A	0
A ^m A ^r A	$\delta^A + \sigma_1^A$ ^a	A ^m M ^m A	$\delta^M + \sigma_1^M$ ^{b,c,d}
A ^m A ^m A	$\delta^A + 2\sigma_1^A$	A ^m M ^m M	$\delta^M + 2\sigma_1^M$
A ^r A ^r M	η^A ^c	A ^r M ^m M	η^M
A ^m A ^r M	$\delta^A + \sigma_1^A + \eta^A$	A ^m M ^r M	$\delta^M + \sigma_1^M + \eta^M$
A ^r A ^m M	$\delta^A + \sigma_1^A + \eta^A$	A ^r M ^m M	$\delta^M + \sigma_1^M + \eta^M$
A ^m A ^m M	$\delta^A + 2\sigma_1^A + \eta^A$	A ^m M ^m M	$\delta^M + 2\sigma_1^M + \eta^M$
M ^r A ^r M	$2\eta^A$	M ^r M ^m M	$2\eta^M$
M ^m A ^r M	$\delta^A + \sigma_1^A + 2\eta^A$	M ^m M ^r M	$\delta^M + \sigma_1^M + 2\eta^M$
M ^m A ^m M	$\delta^A + 2\sigma_1^A + 2\eta^A$	M ^m M ^m M	$\delta^M + 2\sigma_1^M + 2\eta^M$

^a Upper suffix A, acrylonitrile-centered triad.

^b Upper suffix M, methacrylonitrile-centered triad.

^c δ , deshielding effect on CN carbon caused by decreasing ring current of CN triple bond.

^d σ_1 , electron decreasing effect on CN carbon caused by the ring of comeso configuration.

^e η , shift effect on CN carbon to lower magnetic field caused by substitution of methyl group at adjacent copolymer unit.

Table IVb. Reduced relative chemical shifts for ¹³C NMR peaks in CN carbon region of acrylonitrile (A)/methacrylonitrile (M) copolymer

Triad sequence	Relative chemical shift/ppm	Triad sequence	Relative chemical shift/ppm
A ^r A ^r A	0	A M A	0
A ^m A ^r A	0.34	A M M	η^M ^{a,b}
A ^m A ^m A	0.64	M M M	$2\eta^M$
A ^r A ^r M	η^A ^c		
A ^m A ^r M	$\eta^A + 0.34$		
A ^r A ^m M	$\eta^A + 0.34$		
A ^m A ^m M	$\eta^A + 0.64$		
M ^r A ^r M	$2\eta^A$		
M ^m A ^r M	$2\eta^A + 0.34$		
M ^m A ^m M	$2\eta^A + 0.64$		

^a Upper suffix M, methacrylonitrile-centered triad.

^b η , increasing effect of chemical shift caused by substitution of methyl group at adjacent copolymer unit.

^c Upper suffix A, acrylonitrile-centered triad.

Table V. Peak assignment of ^{13}C NMR spectrum in CN carbon region for acrylonitrile (A)/methacrylonitrile (M) copolymer

Peak number in Figure 3	Chemical shifts/ppm	Peak assignment
1	119.4—5	A'A'A
2	119.7—8	A ^m A'A
3	120.0—1	A'A'M, A ^m A ^m A
4	120.3—4	A ^m A'M, A'A ^m M
5	120.7—8	M'A'M, A ^m A ^m M
6	121.10	M ^m A'M
7	121.40	M ^m A ^m M
8	121.77	A ^m M ^m A, A ^m M'A, A'M'A
9	122.42	A ^m M ^m M, A ^m M'M, A'M ^m M, A'M'M
10	123.07	M ^m M ^m M, M ^m M'M, M'M'M

peaks in ^{13}C NMR spectra of AN/MAN copolymers as shown in Figure 1 with copolymer content, peaks 8, 9, and 10 can be attributed to three MAN-centered triads. $\eta^A = 0.64$ and $\eta^M \neq 0$ are thus derived. Finally, assignment can be made for 10 peaks in Figure 2 as shown in Table V.

Mole fractions of triad sequences for sample RMN3 were evaluated from 10 peaks in Figure 2 and collected in the second column of Table VI.

Twenty triad of AN/MAN copolymers are observed, due to heavy overlapping, as 10 peaks in the CN region of ^{13}C NMR spectrum. Therefore, all independent parameter needed to describe 13 statistical models, can be principally determined from the relative intensities of the above 10 peaks. Note that the number of independent parameters varies from 2 to 8, depending on the model employed (see, Table II). The best set of parameters was determined so as to minimize δ' in eq 15. Minimum δ' thus calculated is referred to as δ'_{\min} . This is an extension of Kamide *et al.*'s "alternative method," in which only two parameters are determined.²¹

Table VII summarizes the values of δ'_{\min} for various (in this case 13) combinations of statistical models. In the table, the results

Table VI. Comparison of observed triad fractions of acrylonitrile (A)/methacrylonitrile (M) [sample RMN3], evaluated by direct analysis on ^{13}C NMR spectrum, with those calculated on the basis of [2nd order Markov]–[Bernoulli](non-correlation) statistics using optimized statistical parameters

Triad sequence	Mole fraction	
	Observed	Optimized ^a
(A'A'A)	0.011	0.013
(A ^m A'A)	0.029	0.030
(A'A'M)+(A ^m A ^m A)	0.066	0.065
(A ^m A'M)+(A'A ^m M)	0.110	0.111
(M'A'M)+(A ^m A ^m M)	0.103	0.097
(M ^m A'M)	0.082	0.077
(M ^m A ^m M)	0.042	0.044
(A ^m M ^m A)+(A ^m M'A)+(A'M'A)	0.125	0.129
(A ^m M ^m M)+(A ^m M'M)+(A'M ^m M)	0.270	0.268
(M ^m M ^m M)+(M ^m M'M)+(M'M'M)	0.163	0.164
$\delta'_{\min} \times 10^3$ ^b	—	0.980

^a Optimized parameters: $P_{(A/AA)} = 0.348$; $P_{(A/AM)} = 0.487$; $P_{(A/MA)} = 0.420$; $P_{(A/MM)} = 0.455$; $P_m = 0.537$.

^b δ'_{\min} is minimized value of δ' defined by eq 15 (in this case $N = 10$).

obtained by σ -parameter model ([1st order Markov]–[Bernoulli]) are included for comparison, in which model $\sigma_{AB} = \sigma_{BA}$ is reasonably assumed and 6 parameters, P_A , $P_{(A/A)}$, $P_{(A/B)}$, σ_{AA} , σ_{AB} , and σ_{BB} , are independent. From the table, the most probable combination of statistics can be readily determined for each sample. For sample code RMN3 (radical copolymer), [2nd order Markov]–[Bernoulli](non-correlation), for sample code AMN2 (anionic copolymer) [2nd order Markov]–[1st order Markov](non-correlation), for sample code AMN3 (anionic copolymer) [Bernoulli]–[1st order Markov](correlation), and for sample code AMN9 (anionic copolymer) [2nd order Markov]–[1st order Markov](non-correlation). In this case the uncertainty in δ'_{\min} is expected to be ± 0.01 and then, when the values of δ'_{\min} for two or three combinations lie within ± 0.01 we chose more simple

Table VII. Parameter $\delta'_{\min} \times 10^3$ ^a evaluated for various statistics on acrylonitrile/methacrylonitrile copolymer samples

Sample code	Parameter $\delta'_{\min} \times 10^3$							
	Statistical models presented in this article						σ -Parameter model	
	Cotacticity	Now-correlation			Cotacticity	Correlation		Correlation
		Monomer sequence ^b				Monomer sequence	Monomer sequence	
Bernoulli	1st M		2nd M ^c	Bernoulli	1st M			1st M
RMN3	Bernoulli	2.75	1.70	0.98 ^d	Bernoulli	2.27	1.32	2.01
	1st M	2.70	1.69	0.97	1st M	1.04	—	
	2nd M	2.70	1.69	0.97				
AMN2	Bernoulli	8.14	5.45	4.89	Bernoulli	7.87	5.19	4.30
	1st M	6.86	3.33	2.31	1st M	6.58	—	
	2nd M	6.86	3.33	2.31				
AMN3	Bernoulli	14.21	13.49	13.43	Bernoulli	12.23	11.22	6.65
	1st M	9.14	8.15	7.80	1st M	4.88	—	
	2nd M	9.14	8.15	7.80				
AMN9	Bernoulli	15.69	6.24	4.28	Bernoulli	15.61	5.17	4.36
	1st M	15.53	6.04	3.36	1st M	12.68	—	
	2nd M	15.53	6.04	3.36				

^a δ'_{\min} is minimized value of δ' defined by eq 15 (in this case $N=10$). Results for all samples are not shown here.

^b Monomer sequence, monomer unit sequence.

^c 1st M and 2nd M mean 1st and 2nd order Markov statistics, respectively.

^d \square means the most adequate statistics.

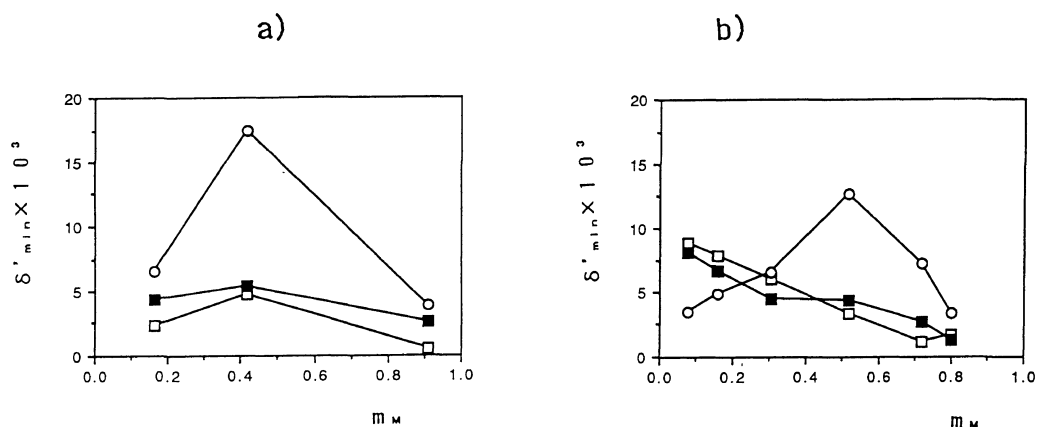


Figure 4. Plots of minimized parameter δ'_{\min} for [2nd order markov]-[1st order Markov](non-correlation), [Bernoulli]-[1st order Markov](correlation) and σ -parameter model vs. mole fraction (m_M) of methacrylonitrile unit in acrylonitrile/methacrylonitrile copolymer: polymerized a) at -77°C ; b) 120°C , both using an anionic catalyst: \square , [2nd order markov]-[1st order Markov](non-correlation); \circ , [Bernoulli]-[1st order Markov](correlation); \blacksquare , σ -parameter model (correlation).

statistical model as the most probable.

Figure 4a) and 4b) show plots of parameters δ'_{\min} as a function of the mole fraction of the MAN monomer unit m_M in the copolymer. Here, δ'_{\min} is δ' corresponding to the best combination of independent parameters for a given statistical model and is calculated for three models: [2nd order Markov]–[1st order Markov](non-correlation), [Bernoulli]–[1st order Markov](correlation), and σ -parameter model (correlation). At low polymerization temperature [2nd order Markov]–[1st order Markov](non-correlation) gives the minimum value of δ'_{\min} over whole range of MAN composition m_M . In contrast, at high polymerization temperature the minimum δ'_{\min} is obtained for [2nd order Markov]–[1st order Markov](non-correlation) at $m_M > 0.3$ and for [Bernoulli]–[1st order Markov](correlation) at $m_M < 0.3$. This implies that at high temperature, the reactivity of AN monomer depends only on cotacticity between the monomer unit of the growing chain end (ultimate monomer unit) and its nearest neighbor monomer unit (penultimate monomer unit), and is independent of monomer unit sequence. The patterns of reaction of AN monomer at low temperature and the MAN monomer at all range of temperature are governed by the monomer unit sequence and cotacticity, both formed between ultimate and penultimate monomer units.

Table VIII collects the statistical parameters for each copolymer sample. Since $P_{(A/AA)}$,

$P_{(A/AM)}$, $P_{(A/MA)}$, and $P_{(A/MM)}$ are all less than 0.5, MAN is more reactive than AN in radical polymerization, but in anionic polymerization, the reactivity of AN becomes higher if AN monomer unit is within ultimate or penultimate units.

The monomer reactivity ratios r_A , r'_A , r_B , and r'_B can be defined by the following equations²⁷:

$$r_A = k_{AAA}/k_{AAB} = P_{(A/AA)}/(1 - P_{(A/AA)})/x \quad (16a)$$

$$r'_A = k_{BAA}/k_{BAB} = P_{(A/BA)}/(1 - P_{(A/BA)})/x \quad (16b)$$

$$r'_B = k_{ABB}/k_{ABA} = (1 - P_{(A/AB)})x/P_{(A/AB)} \quad (16c)$$

$$r_B = k_{BBB}/k_{BBA} = (1 - P_{(A/BB)})x/P_{(A/BB)} \quad (16d)$$

where k_{AAB} is the rate constant of the addition reaction of monomer unit B to the chain ending in AA and k with other suffixes has analogous meaning. The letter x is the molar feed ratio of the monomer A to monomer B.

We define the following parameters r_1 – r_4 by the relations,

$$r_1 = P_{(mA/m)}/P_{(rA/m)} \quad (17a)$$

$$r_2 = P_{(mM/m)}/P_{(rM/m)} \quad (17b)$$

$$r_3 = P_{(mA/r)}/P_{(rA/r)} \quad (17c)$$

$$r_4 = P_{(mM/r)}/P_{(rM/r)} \quad (17d)$$

to demonstrate additive ratio of meso-type arrangement of each monomer to racemo-type one in addition to same configuration of growing chain end.

In Table IX monomer reactivity ratios r_A , r'_A , r_B , and r'_B and the ratios r_1 – r_4 for three

Table VIII. The most probable statistical probabilities determined experimentally for four acrylonitrile (A)/methacrylonitrile (M) copolymer samples

Sample code	Statistical probabilities														
	$P_{(A/AA)}$	$P_{(A/AM)}$	$P_{(A/MA)}$	$P_{(A/MM)}$	P_m	$P_{(r/m)}$	$P_{(m/r)}$	$P_{(mA/m)}$	$P_{(rA/m)}$	$P_{(mM/m)}$	$P_{(rM/m)}$	$P_{(mA/r)}$	$P_{(rA/r)}$	$P_{(mM/r)}$	$P_{(rM/r)}$
RMN3	0.348	0.487	0.420	0.455	0.537	— ^a	—	—	—	—	—	—	—	—	—
AMN2	0.854	0.964	0.668	0.455	—	0.400	0.489	—	—	—	—	—	—	—	—
AMN3	—	—	—	—	—	—	—	0.670	0.222	0.002	0.106	0.338	0.515	0.147	0.000
AMN9	0.604	0.806	0.448	0.234	—	0.379	0.445	—	—	—	—	—	—	—	—

^a Not evaluated.

Table IX. Monomer reactivity ratio and stereoselectivity of acrylonitrile (A)/methacrylonitrile (M) evaluated for three A/M copolymer samples

Sample code	Monomer reactivity ratio ^a				Stereoselectivity ^b			
	r_A	r'_A	r'_M	r_M	r_1	r_2	r_3	r_4
RMN3	0.419	0.569	1.341	1.525	—	—	—	—
AMN2	52.64	18.11	0.00415	0.133	—	—	—	—
AMN3	—	—	—	—	3.018	0.0189	0.656	∞

^a Determined by eq 16a—16d.^b Determined by eq 17a—17d.**Table X.** Triad sequence of acrylonitrile (A)/methacrylonitrile (M) copolymers

Sample code	Method	Triad sequence								
		Monomer unit						Cotacticity		
		(AAA)	(AAM)	(AMA)	(AMM)	(MAM)	(MMM) ^a	$(mm)_c$	$(mr)_c$	$(rr)_c$ ^b
RMN3	A ^c	0.058	0.224	0.128	0.273	0.150	0.167	0.289	0.501	0.210
	B ^d	0.060	0.223	0.129	0.272	0.153	0.163	0.288	0.497	0.215
AMN2	A	0.598	0.195	0.140	0.012	0.049	0.006	0.341	0.437	0.222
	B	0.578	0.200	0.145	0.011	0.049	0.006	0.330	0.440	0.230
AMN3	A	0.671	0.194	0.094	0.026	0.013	0.002	0.412	0.383	0.205
	B	0.674	0.189	0.093	0.027	0.013	0.002	0.400	0.390	0.210

^a (AAA), (AAM), (AMA), (AMM), (MAM), and (MMM) are calculated from eq 11a—11f.^b $(mm)_c$, $(mr)_c$, and $(rr)_c$ are calculated from eq 12a, 12d, and 12g.^c Method A: mean mole fractions for 10^4 copolymer chains hypothetically generated with computer by Monte Carlo method using the most probable statistical probabilities determined experimentally.^d Method B: mean mole fractions calculated from eq 11a—11f and eq 12a—12i, using the most probable statistical probabilities determined experimentally.

samples are summarized. For sample code AMN3, the reactivity of AN monomer to the growing chain, whose end is comeso configuration, to yield the new end with comeso configuration is three times larger than that of the chain resulting in a coracemo configuration. In contrast, MAN is less reactive to the growing chain which end has the comeso configuration, than to the chain which end the coracemo configuration. But when MAN is added to the chain with a comeso end, the new coracemo end brings about with large possibility. It is interesting to note that there is no chance of adding MAN monomer to the chain with a

coracemo end to yield new coracemo configuration as chain end.

AN/MAN copolymer chains with the degree of polymerization (number of all kinds of monomers consisting a chain) as 10^3 were hypothetically synthesized in a electronic computer by the Monte Carlo method using the most probable parameters of the best fit statistical model for samples (Table VIII). Here, the following three samples are chosen: sample RMN3 as the sample prepared radical polymerization, AMN2 and AMN3 as samples polymerized at low and high temperature by anionic polymerization, respectively.

Sequence Distribution of AN/MAN Copolymer

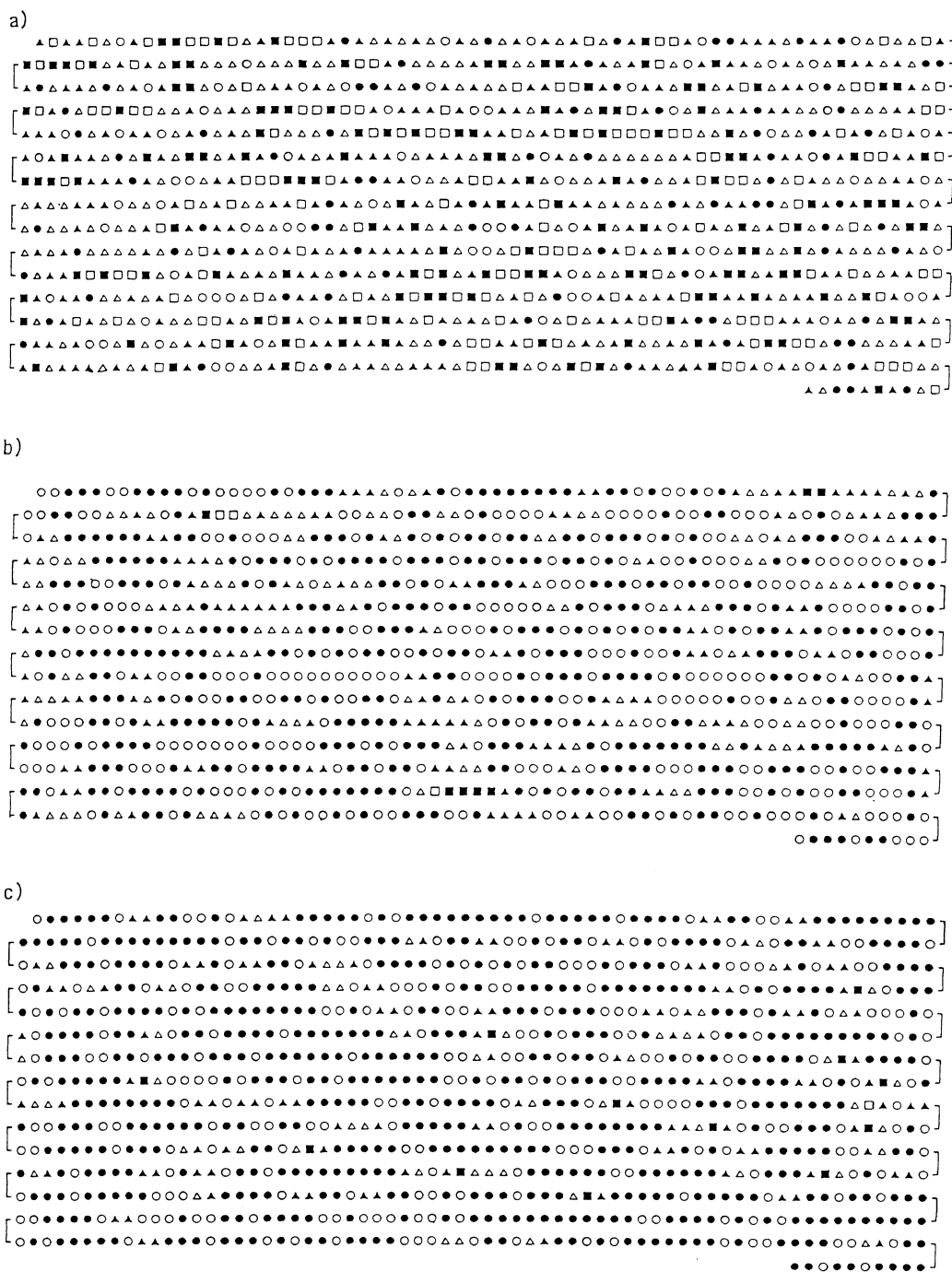


Figure 5. Examples of three acrylonitrile/methacrylonitrile copolymer samples generated by the Monte Carlo simulation method: a), RMN3 (polymerized radically at 60°C); b), AMN2 (polymerized anionically at -77°C); c), AMN3 (polymerized anionically at 120°C); ●, AN-AN comeso diad; ○, AN-AN coracemo diad; ▲, AN-MAN comeso diad; △, AN-MAN coracemo diad; ■, MAN-MAN comeso diad; □, MAN-MAN coracemo diad.

Table XI. Mean length of acrylonitrile (A) or methacrylonitrile (M) (e.g., AA···A or MM···M), comeso and coracemo sequence (e.g., *mm*···*m* or *rr*···*r*) and mole fractions A and M in A/M copolymer

Sample code	Method	Mean length				Mole fraction	
		Number of monomer unit		Number of diad		A	M
		AA···A	MM···M	<i>mm</i> ··· <i>m</i>	<i>rr</i> ··· <i>r</i>		
RMN3	A ^a	1.644	2.144	2.136	1.879	0.434	0.566
	B ^b	1.648	2.128	2.159	1.865	0.436	0.564
AMN2	A	5.623	1.071	2.531	2.033	0.844	0.160
	B	5.611	1.076	2.500	2.045	0.836	0.164
AMN3	A	8.501	1.141	3.025	2.068	0.880	0.119
	B	8.423	1.146	3.051	2.077	0.876	0.124

^a Method A (see Table IX).

^b Method B: calculated through eq 13a, 13b, 14a, and 14b, using the most probable statistical probabilities determined experimentally.

In order to visualize the sequence distribution AN/MAN copolymer, the number (in this case, 10^4 for each sample) of AN/MAN copolymer chains with copolymer triad sequences giving the statistical parameters (Table VIII), were generated hypothetically by the Monte Carlo method using an electronic computer (see, Figure 5). The details of the procedure are almost the same as those first established by Kamide *et al.*⁶

Table X summarizes the mean mole fraction of six triad monomer unit sequences AAA, AAM, AMA, AMM, MAM, and MMM and those of three triad cotacticities *mm*, *mr*, and *rr* for the three AN/MAN copolymers. The values shown in the upper rows of each samples in the table are average values of hypothetically synthesized copolymer (10^4 chains for each samples). Those in the lower rows are values calculated directly from eq 11a—11i. The introduction of MAN has a tendency to decrease stereoregularity at higher polymerization temperature in anionic polymerization. From the table, the triad coisotacticity (*mm* fraction) was found to be 0.289, 0.341, and 0.412 for sample codes RMN3, AMN2, and AMN3, respectively. It is very interesting that

the tendency of stereoregularity of AN/MAN copolymers synthesized by radical, high and low temperature polymerizations is similar to that of homopolyacrylonitriles prepared by respective conditions, which are reported by Kamide *et al.*¹⁸

Table XI shows the mean length of monomer unit sequences (*i.e.*, AA···A or MM···M) and the mean length of cotacticity sequences (*i.e.*, *mm*···*m* or *rr*···*r*) for the above three copolymer samples. Here, mean length was determined by computer simulation and using eq 13a, 13b, 14a, and 14b. The AN monomer sequence is longer in the copolymer prepared by anionic polymerization than in the copolymer by radical polymerization and in the former case, the copolymer polymerized at higher temperature gives longer AN monomer sequences. The mean length of two kinds of cotacticity sequences is longer in the anionic than radical copolymer and the mean length of *mm*···*m* sequence is longer at higher polymerization temperature.

CONCLUSION

- 1) Assuming for bi-component copolymers

that the propagation reaction is fully explained by combination of statistics, in which both monomer units have the possibility of yielding stereoregular homopolymer sequence, one controlling monomer unit sequence and the other its cotacticity, we derived a theory for the determination of copolymer sequence distribution. The applicability of the theory was examined by AN/MAN copolymers.

2) ^{13}C NMR peaks in CN carbon region of AN/MAN copolymer were successfully assigned with help of the method originally employed by Kamide *et al.*²⁴ for PAN.

3) The copolymer sequence distribution of radical AN/MAN copolymer can be well explained as a combined process of 2nd order Markov for monomer unit sequence and Bernoulli for its cotacticity (both statistics have no correlation). Monomer unit sequence and its cotacticity of anionic AN/MAN copolymer, prepared at low temperature, can be represented by 2nd order Markov and 1st order Markov processes, respectively (both statistics have no correlation).

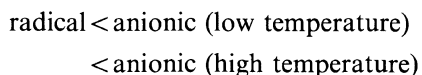
Copolymer sequence distribution of the anionic AN/MAN copolymer, polymerized at high temperature and containing higher molar content of MAN than 0.3, can be explained by a combined process of 2nd order Markov for a monomer unit sequence and 1st order Markov for cotacticity (both statistics have no correlation), but for copolymers containing higher AN content than 0.7 prepared under similar conditions, copolymer sequence distribution can be reasonably approximated with a combined process of Bernoulli for monomer unit sequence and 1st order Markov for its cotacticity (both statistics have correlation). Over the entire region of copolymer content, the σ -parameter model is not the most suitable.

4) The monomer reactivity ratio, estimated from the above statistical parameters, differed greatly depending on the polymerization method employed.

5) Using the best fit statistical parameters, 10^4 copolymer molecules were hypothetically

generated for each sample by Monte Carlo simulation and the most probable molecular structures of these samples were visualized.

6) Coisotacticity of AN/MAN copolymer increased in the order:



APPENDIX

Mole Fractions of Triad Sequence

(A) Non-Correlation Case.

The subcase A2 where monomer unit sequence distribution obeys 1st Markov statistics and its cotacticity distribution obeys Bernoulli statistics ([1st order Markov]–[Bernoulli](non-correlation)):

If $P_{(A/B)}$ is referred to as the probability for the addition of monomer unit A to the growing chain end in monomer B, and $P_{(B/A)} + P_{(A/B)}$ is shortly referred to as Y , the mole fractions of 20 different triad copolymer sequences are:

$$(A^m A^m A) = (1 - P_{(B/A)})^2 P_{(A/B)} P_m^2 / Y \quad (\text{A.1a})$$

$$(A^m A^r A) = 2(1 - P_{(B/A)})^2 P_{(A/B)} P_m (1 - P_m) / Y \quad (\text{A.1b})$$

$$(A^r A^r A) = (1 - P_{(B/A)})^2 P_{(A/B)} (1 - P_m)^2 / Y \quad (\text{A.1c})$$

$$(A^m A^m B) = 2P_{(B/A)} (1 - P_{(B/A)}) P_{(A/B)} P_m^2 / Y \quad (\text{A.2a})$$

$$(A^m A^r B) = 2P_{(B/A)} (1 - P_{(B/A)}) P_{(A/B)} P_m (1 - P_m) / Y \quad (\text{A.2b})$$

$$(A^r A^m B) = 2P_{(B/A)} (1 - P_{(B/A)}) P_{(A/B)} P_m (1 - P_m) / Y \quad (\text{A.2c})$$

$$(A^r A^r B) = 2P_{(B/A)} (1 - P_{(B/A)}) P_{(A/B)} (1 - P_m)^2 / Y \quad (\text{A.2d})$$

$$(B^m A^m B) = P_{(B/A)}^2 P_{(A/B)} P_m^2 / Y \quad (\text{A.3a})$$

$$(B^m A^r B) = 2P_{(B/A)}^2 P_{(A/B)} P_m (1 - P_m) / Y \quad (\text{A.3b})$$

$$(B^r A^r B) = P_{(B/A)}^2 P_{(A/B)} (1 - P_m)^2 / Y \quad (\text{A.3c})$$

$$(A^m B^m A) = P_{(B/A)} P_{(A/B)}^2 P_m^2 / Y \quad (\text{A.4a})$$

$$(A^m B^r A) = 2P_{(B/A)} P_{(A/B)}^2 P_m (1 - P_m) / Y \quad (\text{A.4b})$$

$$(A^r B^r A) = P_{(B/A)} P_{(A/B)}^2 (1 - P_m)^2 / Y \quad (\text{A.4c}) \quad (A^r A^r A) = P_{(A/B)} P_{(rA/A)}^2 / Y \quad (\text{A.8c})$$

$$(A^m B^m B) = 2P_{(B/A)} P_{(A/B)} (1 - P_{(A/B)}) P_m^2 / Y \quad (\text{A.5a}) \quad (A^m A^m B) = (P_{(A/B)} P_{(mA/A)} P_{(mB/A)} + P_{(B/A)} P_{(mA/B)} P_{(mA/A)}) / Y \quad (\text{A.9a})$$

$$(A^m B^r B) = 2P_{(B/A)} P_{(A/B)} (1 - P_{(A/B)}) P_m (1 - P_m) / Y \quad (\text{A.5b}) \quad (A^m A^r B) = (P_{(A/B)} P_{(mA/A)} P_{(rB/A)} + P_{(B/A)} P_{(rA/B)} P_{(mA/A)}) / Y \quad (\text{A.9b})$$

$$(A^r B^m B) = 2P_{(B/A)} P_{(A/B)} (1 - P_{(A/B)}) P_m (1 - P_m) / Y \quad (\text{A.5c}) \quad (A^r A^m B) = (P_{(A/B)} P_{(rA/A)} P_{(mB/A)} + P_{(B/A)} P_{(mA/B)} P_{(rA/A)}) / Y \quad (\text{A.9c})$$

$$(A^r B^r B) = 2P_{(B/A)} P_{(A/B)} (1 - P_{(A/B)}) (1 - P_m)^2 / Y \quad (\text{A.5d}) \quad (A^r A^r B) = (P_{(A/B)} P_{(rA/A)} P_{(rB/A)} + P_{(B/A)} P_{(rA/B)} P_{(rA/A)}) / Y \quad (\text{A.9d})$$

$$(B^m B^m B) = P_{(B/A)} (1 - P_{(A/B)})^2 P_m^2 / Y \quad (\text{A.6a}) \quad (B^m A^m B) = P_{(B/A)} P_{(mA/B)} P_{(mB/A)} / Y \quad (\text{A.10a})$$

$$(B^m B^r B) = 2P_{(B/A)} (1 - P_{(A/B)})^2 P_m (1 - P_m) / Y \quad (\text{A.6b}) \quad (B^m A^r B) = P_{(B/A)} (P_{(mA/B)} P_{(rB/A)} + P_{(rA/B)} P_{(mB/A)}) / Y \quad (\text{A.10b})$$

$$(B^r B^r B) = P_{(B/A)} (1 - P_{(A/B)})^2 (1 - P_m)^2 / Y \quad (\text{A.6c}) \quad (B^r A^r B) = P_{(B/A)} P_{(rA/B)} P_{(rB/A)} / Y \quad (\text{A.10c})$$

$$(B^r A^r B) = P_{(B/A)} P_{(rA/B)} P_{(rB/A)} / Y \quad (\text{A.10c})$$

$$(A^m B^m A) = P_{(B/A)} P_{(mB/A)} P_{(mA/B)} / Y \quad (\text{A.11a})$$

$$(A^m B^r A) = P_{(A/B)} (P_{(mB/A)} P_{(rA/B)} + P_{(rB/A)} P_{(mA/B)}) / Y \quad (\text{A.11b})$$

$$(A^r B^r A) = P_{(A/B)} P_{(rB/A)} P_{(rA/B)} / Y \quad (\text{A.11c})$$

$$(A^m B^m B) = (P_{(A/B)} P_{(mB/A)} P_{(mB/B)} + P_{(B/A)} P_{(mB/B)} P_{(mA/B)}) / Y \quad (\text{A.12a})$$

$$(A^m B^r B) = (P_{(A/B)} P_{(mB/A)} P_{(rB/B)} + P_{(B/A)} P_{(rB/B)} P_{(mA/B)}) / Y \quad (\text{A.12b})$$

$$(A^r B^m B) = (P_{(A/B)} P_{(rB/A)} P_{(mB/B)} + P_{(B/A)} P_{(mB/B)} P_{(rA/B)}) / Y \quad (\text{A.12c})$$

$$(A^r B^r B) = (P_{(A/B)} P_{(rB/A)} P_{(rB/B)} + P_{(B/A)} P_{(rB/B)} P_{(rA/B)}) / Y \quad (\text{A.12d})$$

$$(B^m B^m B) = P_{(B/A)} P_{(mB/B)}^2 / Y \quad (\text{A.13a})$$

$$(B^m B^r B) = 2P_{(B/A)} P_{(mB/B)} P_{(rB/B)} / Y \quad (\text{A.13b})$$

$$(B^r B^r B) = P_{(B/A)} P_{(rB/B)}^2 / Y \quad (\text{A.13c})$$

Also in this subcase $P_{(B/A)} = P_{(mB/A)} + P_{(rB/A)}$ and $P_{(A/B)} = P_{(mA/B)} + P_{(rA/B)}$ hold. The mole fractions of 20 triad copolymer sequences are:

$$(A^m A^m A) = P_{(A/B)} P_{(mA/A)}^2 / Y \quad (\text{A.8a})$$

$$(A^m A^r A) = 2P_{(A/B)} P_{(mA/A)} P_{(rA/A)} / Y \quad (\text{A.8b})$$

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