Intramolecular Reaction between Neighboring Substituents of Specially-Designed Alternating Copolymers

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ABSTRACT: The maximum conversion of an intramolecular reaction between neighboring substituents on specially-designed alternating copolymers was calculated theoretically. The terpolymer of monomers A, D₁, and D₂, were supposed to consist of two alternating units, A-D₁ and A-D₂, distributed in a certain statistical state. In such a modified alternating copolymer, substituent X on unit A was permitted to perform the intramolecular reaction only with substituent Y₁ on unit D₁, not with Y₂ on D₂. As a result, the theoretical maximum conversion could be expressed as a function of a mole fraction of A-D₁. If these alternating units were arranged as alternatively as possible, the best conversion near to 100% could be achieved over a wide range of the A-D₁ fraction. Even if the arrangement was random, a considerably good conversion beyond 86.5% could still be expected. However, the blocky arrangement resulted in limiting the yield to 86.5% (Flory's limit) which was equal to the statistically possible level in the simple alternating copolymer of A and D₁.

KEY WORDS Intramolecular Reaction / Terpolymer / Alternating Copolymer / Maximum Conversion / Flory's Limit / Statistics /

Recently, various alternating copolymers have been obtainable from electron-accepting-type and electron-donating-type monomers, often by using Lewis acids.¹⁻⁴ These copolymers have two different substituents, X and Y, alternately on every third carbon of the copolymer chain. This seems advantageous when making an attempt to these substituents into polymers having a new structure Z through an intramolecular reaction between X and Y.

Flory considered statistically the theoretical maximum conversion for the intramolecular reaction of pairs of consecutive substituents X on the polymer composed of -CH₂CHX- units.⁵ According to his consideration, even for the alternating copolymers, the theoretical maximum conversion is 86.5% (the so-called Flory's limit) and 13.5% of either X or Y is prevented from reacting due to isolation among the reacted pairs.

In this paper, the authors show theoretically that the substituent Y on a specially-designed alternating copolymer can undergo an intramolecular reaction with the substituent X to an extent beyond the Flory's limit.

THEORETICAL

Specially-Designed Alternating Copolymer and Its Intramolecular Reaction

Suppose that a monomer A (substituent X) can copolymerize alternately with either a monomer D₁ (substituent Y₁) or a monomer D₂ (substituent Y₂). The ternary copolymerization of A, D₁, and D₂ under favorable conditions for alternating copolymerization yields a copolymer in which the mole fraction of A equals the sum of the mole fractions of D₁ and D₂, as is often shown by examples in the literatures.^{6,7} Thus every A unit in the copolymer is neighbored by either a D₁ unit or D₂ unit. In other words, this terpolymer can be regarded as a copolymer consisting of two alternating units, A-D₁ and A-D₂.

Also, suppose that the substituent X can perform an intramolecular reaction only with the substituent Y_1 but not with the substituent Y_2 . The intramolecular reaction between X and the remote Y_1 deviating from the 1,3-position on the copolymer chain may be disregarded. Thus the substituent Y_1 on an A-D₁ unit whose neighbors are both A-D₂ units is bound to react with one of the neighboring substituents X, whereas the substituent Y_1 on an A-D₁ unit whose neighbors are also both A-D₁ units may or may not react, this being left to statistical chance.

In order to calculate statistically the maximum conversion based on Y_1 for its intramolecular reaction with X on the alternating copolymer mentioned above, we divide the copolymer molecules into sequences according to the number of successive A-D₁ units. Each sequence ends with one A-D₂ unit. The number of the sequence- i ($i=0, 1, 2, \dots$) which contains successively i members of A-D₁ units is denoted by P_i . A visible relationship among them is illustrated in Table I.

Definition of the Theoretical Maximum Conversion

Let N_x be the total number of A-D₁ units and N_y be the total number of A-D₂ units in the original copolymer molecules. Consequently, N_x and N_y also equal the total number of substituents Y_1 and Y_2 , respectively. Then,

$$N_x = \sum_{i=0} i P_i \quad (1)$$

and

$$N_y = \sum_{i=0} P_i \quad (2)$$

When the average number of Y_1 , statistically remaining unreacted following the intramolecular reaction of Y_1 with X on the sequence- i , is defined by S_i , the total number of Y_1 statistically remaining unreacted, N_r , is given by eq 3,

$$N_r = \sum_{i=0} S_i P_i \quad (3)$$

and the ratio of Y_1 remaining unreacted to the total number of Y_1 in the original copolymer is given by

$$R = N_r/N_x = \sum_{i=0} S_i P_i / \sum_{i=0} i P_i \quad (4)$$

The theoretical maximum conversion, f , is defined

Table I. Specification of sequences in the specially-designed copolymer

Sequence- i	Structure of the sequence- i	Number of the sequence- i
$i=0$	(A-D ₂)	P_0
1	(A-D ₁)-(A-D ₂)	P_1
2	(A-D ₁)-(A-D ₁)-(A-D ₂)	P_2
.	.	.
.	.	.
.	.	.
i	$\underbrace{(A-D_1) - \dots - (A-D_1)}_i - (A-D_2)$	P_i
.	.	.
.	.	.
.	.	.

as

$$f = 1 - R \quad (5)$$

The Most Probable Distribution of A-D₁ and A-D₂ Units

We now consider the distribution of A-D₁ and A-D₂ units. First we deal with the copolymer in which all A-D₁ and A-D₂ are randomly distributed under the control of the probability factor alone. Other special cases will be discussed later.

The number of complexions in the statistical state represented by $P_0, P_1, P_2, \dots$ is given by

$$W = N_y! / P_0! P_1! P_2! \dots \quad (6)$$

The most probable distribution state corresponds to the maximum value for W . Thus, this problem can be treated in a manner similar to that for deriving the Maxwell-Boltzmann distribution law.⁸ Applying Stirling's approximation to $\ln W$ and setting its variation equal to zero, we have,

$$\delta \ln W = - \sum_{i=0} \ln P_i \delta P_i = 0 \quad (7)$$

Equation 7 is, however, subject to two additional equations obtained by taking variations of equations 1 and 2,

$$\delta N_x = \sum_{i=0} i \delta P_i = 0 \quad (8)$$

$$\delta N_y = \sum_{i=0} \delta P_i = 0 \quad (9)$$

Introducing Lagrangian multipliers to express P_i under these conditions 7-9 and combining mathematically, we find that

$$P_i = e^{-\lambda - \mu i} \quad (10)$$

Substituting eq 10 into eq 1 and 2 to determine λ and μ , we obtain

$$N_x = \sum_{i=0}^{\infty} i e^{-\lambda - \mu i} = e^{-\lambda - \mu} / (1 - e^{-\mu})^2 \quad (11)$$

$$N_y = \sum_{i=0}^{\infty} e^{-\lambda - \mu i} = e^{-\lambda} / (1 - e^{-\mu}) \quad (12)$$

Consequently, eq 10 can be now expressed as

$$P_i = \{N_y^2 / (N_x + N_y)\} \{N_x / (N_x + N_y)\}^i \quad (13)$$

Taking into account the mole fraction of A-D₁ and A-D₂ units in the modified alternating copolymer, (A-D₁)_x(A-D₂)_y, we know that

$$N_x / (N_x + N_y) = x,$$

$$N_y / (N_x + N_y) = y = 1 - x$$

and therefore that,

$$P_i = N_x (1 - x)^2 x^{i-1} \quad (14)$$

Then eq 4 defining R , can be rewritten as

$$R = \sum_{i=0}^{\infty} S_i (1 - x)^2 x^{i-1} \quad (15)$$

Expanding and rearranging,

$$\begin{aligned} &= \sum_i S_i (x^{i+1} - 2x^i + x^{i-1}) \\ &= \sum_i (S_{i+1} - 2S_i + S_{i-1}) x^i \end{aligned} \quad (16)$$

and defining $\Delta_i = S_i - S_{i-1}$, ($i \geq 1$), we obtain

$$R = \sum_i (\Delta_{i+1} - \Delta_i) x^i \quad (17)$$

This equation requires an evaluation of S_i , the average number of substituent Y_1 statistically remaining unreacted following the intramolecular reaction on the sequence- i in order to embody numerals of R .

Statistical Evaluation of S_i Value

If it is assumed that the probability of an intramolecular reaction for any adjacent pairs of unreacted substituents X and Y_1 is the same and independent of the status of other neighbors, a series of numbers $\{S_i\}$ can be evaluated systematically

with the assistance of two supplementary progressions, $\{S_i'\}$ and $\{S_i''\}$. Here, S_i' and S_i'' mean the average numbers of Y_1 statistically remaining unreacted at the end of the intramolecular reaction on the following fragments.

(i) $\{S_i\}$ series

S_0 for a fragment	A
S_1	A-D ₁ -A
S_2	A-D ₁ -A-D ₁ -A
.	.
.	.
.	.
S_n	A-(D ₁ -A) _n

(ii) $\{S_i'\}$ series

S_0' for a fragment	—
S_1'	A-D ₁
S_2'	A-D ₁ -A-D ₁
.	.
.	.
.	.
S_n'	(A-D ₁) _n

(iii) $\{A_i''\}$ series

S_0'' for a fragment	D ₁
S_1''	D ₁ -A-D ₁
S_2''	D ₁ -A-D ₁ -A-D ₁
.	.
.	.
.	.
S_n''	D ₁ -(A-D ₁) _n

It should be kept in mind that the fragments illustrated as $\{S_i\}$ series are equivalent to the structures of the sequence- i 's classified in Table I where these have D₂ units at their terminal positions and that S_0' is a helpful term for formulating relations among S_i , S_i' , and S_i'' ; nevertheless, it is the imaginary term.

Consequently, the following three equations can be obtained: eq 18-20.

$$S_n = \frac{1}{n} \sum_{i=0}^{n-1} (S_i + S_i') \quad n \geq 1, \text{ and } S_0 = 0 \quad (18)$$

$$S_n' = \frac{1}{2n-1} \left\{ \sum_{i=0}^{n-2} (S_i + S_i'') + 2 \sum_{i=0}^{n-1} S_i' \right\} \quad n \geq 2, \text{ and } S_0' = S_1' = 0 \quad (19)$$

$$S_n'' = \frac{1}{n} \sum_{i=0}^{n-1} (S_i'' + S_i') \quad n \geq 1, \text{ and } S_0'' = 1 \quad (20)$$

In eq 18, subtracting nS_n from $(n+1)S_{n+1}$ gives,

$$S_{n+1} - S_n = \frac{1}{n+1} S'_n \quad n \geq 0 \quad (21)$$

By similar treatment for eq 19 and 20, we obtain

$$S'_{n+1} - S'_n = \frac{1}{2n+1} (S_{n-1} + S''_{n-1}) \quad n \geq 1 \quad (22)$$

$$S''_{n+1} - S''_n = \frac{1}{n+1} S'_n \quad n \geq 0 \quad (23)$$

Combining eq 21 and 23 and then using the initial values, we find that

$$S_n = S''_n - 1 \quad n \geq 0 \quad (24)$$

Substitution of eq 24 into 22 gives

$$S'_{n+1} = S'_n + \frac{1}{2n+1} (2S_{n-1} + 1) \quad n \geq 1 \quad (25)$$

Thus, S_i and S'_i can be now evaluated by using eq 21 and 25 in turn with each other.

RESULTS AND DISCUSSION

Table II shows the calculated S_i , Δ_{i+1} , and $\Delta_{i+1} - \Delta_i$ in the range of $8 \geq i \geq 0$. It can be seen from Table II that $R(x)$ described by the eq 17 is given approximately by calculating the progression down to just the fifth term.

$$R(x) = \sum_i (\Delta_{i+1} - \Delta_i) x^i \simeq \sum_{i=1}^5 (\Delta_{i+1} - \Delta_i) x^i \quad (1 \geq x \geq 0) \quad (26)$$

The theoretical maximum conversion, f , can then be expressed as a function of the mole fraction of A-D₁ units, x ,

$$f(x) = 1 - (0.11111 + 0.02222x + 0.00190x^2 + 0.00009x^3)x^2 \quad (27)$$

The full line in Figure 1 shows the dependence of f on x .

In the case of $x=1$, i.e., when we deal with the simple alternating copolymer of A and D₁ units, the theoretical maximum conversion is

$$f(x=1) = 1 - 0.1353 \cdots = 0.8647 \cdots$$

This result is consistent with the limit considered by Flory.

Table II. Values of S_i , Δ_{i+1} , and $\Delta_{i+1} - \Delta_i$

i	S_i	$\Delta_{i+1} = S_{i+1} - S_i$	$\Delta_{i+1} - \Delta_i \ (i \geq 1)$
0	0	0	—
1	0	0	0
2	0	0.1111111	0.1111111
3	0.1111111	0.1333333	0.0222222
4	0.2444444	0.1352381	0.0019048
5	0.3796825	0.1353322	0.0000941
6	0.5150147	0.1353352	3.05×10^{-6}
7	0.6503499	0.1353352	0.07×10^{-6}
8	0.7856851	0.1353352	0.00×10^{-6}

Figure 1. Dependence of the theoretical maximum conversion, f , on the mole fraction of A-D₁ units, in an intramolecular reaction of modified alternating copolymers $(A-D_1)_x(A-D_2)_y$.

As x decreases from 1 to 0, i.e., when we deal with the modified alternating copolymer of A, D₁, and D₂, f increases from 0.8647... to 1. Such a high theoretical conversion beyond the Flory's limit is obviously achieved by the copolymerized D₂ units whose substituent Y₂ can not react with the substituent X on the A unit, because the resulting sequences of A-D₁ units are made relatively short and advantageous for avoiding the isolation of Y₁ in the course of the intramolecular reaction.

The above discussion concerns the statistically

random copolymer of A-D₁ and A-D₂ units. Next we will discuss two other special cases.

(i) *Block Copolymer.* Here we deal with a copolymer containing a few relatively long sequences of A-D₁ or A-D₂ units

In this case, the situation regarding the A-D₁ sequences is identical to that of the simple alternating copolymer of the A and D₁ units. Therefore, the theoretical maximum conversion should be 86.5% in a wide range of x , as shown by the dotted line in Figure 1.

(ii) *Alternating Copolymer.* Here we consider the copolymer containing alternatingly A-D₁ and A-D₂ units, just as

Thus, the substituent Y₁ on D₁ unit can react completely with one of the two neighboring X's on an A unit. Even if the alternating arrangement of the two units is not entirely complete, if the relatively short sequences classified as $3 \geq i \geq 1$ in Table I are dominant in the ternary copolymer, a high conversion near to 100% can be achieved in the wide range of x as shown by the broken line in Figure 1.

Last of all, we compare the specially-designed alternating copolymers of A, D₁, and D₂ with conventional copolymers of A and D ($\equiv$ D₁) units and explain the significance of our design. In an intramolecular reaction between neighboring A and D units on the later copolymer, the total number of D units remaining unreacted following an intramolecular reaction can be estimated roughly by considering the D units inside a triad -DDD-, a pentad -DDADD-, and a heptad -DDADADD-. When the existence probability of the above sequences is denoted as $P(DDD)$, $P(DDADD)$, and $P(DDADADD)$, respectively, the fraction of the D unit remaining unreacted, R' , can be approximated by eq 28 on the premise that the sequence distribution of the copolymer is determined by the Markov-chain process or the Bernoulli trial.

$$R' = \{P(DDD) + P(DDADD) + P(DDADADD)\} / P(D) \quad (28)$$

Here, $P(D)$ is equal to the mole fraction of D units

Figure 2. Dependence of the theoretical maximum conversion, f , on the mole fraction of D units, $P(D)$, in an intramolecular reaction of the simple copolymers of D(M₁) and A(M₂). The curves 1, 2, and 3 correspond the cases of $r_1=0.2$, $r_2=1.6$; $r_1r_2=1$; and $r_1=0.4$, $r_2=6.4$, respectively.

and each probability can be calculated by using a set of monomer-reactivity ratios, $r_1(=k_{DD}/k_{DA})$ and $r_2(=k_{AA}/k_{AD})$, and a given mole ratio of the fed monomers, $[D]/[A]$.⁹

Figure 2 shows the dependence of the theoretical maximum conversion, f , defined by $f=1-R'$, on the mole fraction of D units for the intramolecular reaction on the conventional copolymers. Curves 1 and 3 correspond to the intramolecular reactions between substituents on the copolymers of butyl vinyl ether(D)-methyl methacrylate(A)¹⁰ and allyl chloride(D)-methyl acrylate(A),¹¹ respectively, and curve 2 represents an optional reaction on the copolymer whose sequence distribution is determined by the Bernoulli trial.

According to Figures 1 and 2, we can see that, as to the intramolecular reaction on the copolymers containing the same amount of D($\equiv$ D₁) unit, the maximum conversion of the specially-designed alternating copolymer is superior to that of the other simple copolymers. Though the simple copolymer can also achieve high conversion beyond the 86.5% level by increasing A units, the derived copolymer will become similar to the A polymer itself in terms of physical and chemical properties

and therefore should be distinguished from the specially-designed alternating copolymer.

The advantage of our design is not only that designed copolymers can achieve high conversion near 100% in their intramolecular reaction but also that the various properties of the resulting copolymers can be controlled by using various D₂ units and also by changing the D₂ content as desired.

In the following paper, we will present experimental examples of such modified alternating copolymers.¹²

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