Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Markovian Statistics of Nonhomogeneous Copolymer Systems

James F. Ross[a]
[a] Technical Center, Morris, Illinois

To cite this Article Ross, James F.(1986) 'Markovian Statistics of Nonhomogeneous Copolymer Systems', Journal of Macromolecular Science, Part A, 23: 12, 1443 — 1450

To link to this Article: DOI: 10.1080/00222338608081135

URL: http://dx.doi.org/10.1080/00222338608081135

J. MACROMOL. SCI.–CHEM., A23(12), pp. 1443-1450 (1986)

Markovian Statistics of Nonhomogeneous Copolymer Systems

JAMES F. ROSS

Technical Center
Norchem
Morris, Illinois 60450-9988

ABSTRACT

Nonhomogeneous copolymer systems that follow Markovian kinetics on a microscale will give non-Markovian sequence distributions in the polymer produced. This is because each microdomain is statistically independent of the others and the assumption of statistical stationarity does not apply. Equations that consider nonhomogeneity, however, do apply and can reconcile Markovian kinetics and non-Markovian sequence distributions. Failures of systems to follow lower order Markovian mechanisms based on distribution data should be reviewed for nonhomogeneity. Complex mathematical models that can never be validated experimentally should only be considered if nonhomogeneity fails to explain the data adequately.

INTRODUCTION

For about 40 years the concept of Markov chain statistics has been applied to copolymer systems. This treatment provides a rational, elegant, and mathematically precise explanation of copolymer compositions and sequence distributions in terms of a chain or sequence of conditional probabilities [1].

0022-233X/86/2312-1443$3.50/0

In essence, this technique considers the probability of finding a given sequence in a copolymer, for example, the sequence (wx· · · yx), as the joint probability of incorporating w, incorporating x into a polymer chain that ends with w, . . ., incorporating z into a polymer chain that ends in y. In mathematical notation,

$$P(wx\cdots yx) = P(w)\cdot P(w|x)\cdots P(y|z). \tag{1}$$

These probabilities can be calculated for varying orders of complexity by assuming that the addition of a monomeric unit to a polymer chain is affected by the previous N additions. Equations have been derived for several lower orders of Markov chains [2] (see Table 1).

For some years now, analysis of copolymer sequences has provided a way to verify these models. Sequence analysis by ^{13}C NMR has been made through monomer pentads in some cases. These measured sequence distributions have been compared to theoretically predicted values in order to elucidate basic copolymerization kinetics. Some systems, especially Ziegler-Natta-catalyzed olefin copolymers, often show poor agreement with lower order models. This has been taken as a reason to doubt that a low-order Markovian mechanism applies to these systems [3, 4]. However, nonhomogeneity can account for differences between measured and predicted sequences in low-order Markovian systems [5]. Essentially, this work showed that addition copolymer systems that follow Markovian statistics as viewed by the catalyst cannot be expected, in general, to do so on a larger scale unless the system is completely homogeneous. This is because each microdomain is statistically independent of every other one, and statistical stationarity can hold only within individual microdomains.

Microdomains are defined as single active catalyst sites and their immediate environments considered over a time interval that is a) long enough that the basic assumptions of traditional Markov statistics are satisfied, and b) short enough that both the site and its immediate environment can be considered essentially constant. Variations in time and space are assumed to occur during polymerization. Local

TABLE 1

Order	Model
Zero	Wall
First	Mayo-Lewis
Second	Merz-Alfrey-Goldfinger (Penultimate Model)
Third	Ham (Pen-penultimate Model)

variations that are possible in the present analysis can include 1) multiple catalyst types, 2) multiple steady states, 3) catalyst activation and deactivation, 4) build-up of catalyst poisons, 5) build-up of inert species at the active site, 6) local monomer ratio variations, 7) differential diffusion to the active site, 8) local temperature effects (balance between heat of polymerization and heat removal); in short, any effects that give rise to nonhomogeneities.

If any or all of these effects can influence the course of polymerization at any given microdomain, it follows that each microdomain is statistically independent of every other microdomain whether the same active site undergoes changes with time or different conditions occur at different sites. Granted that what goes on in one microdomain may influence what goes on in another, the influence is indirect, i.e., restricted to altering boundary or initial conditions. Each microdomain independently reacts to, and only to, its own conditions.

Mathematically, for n statistically independent microdomains constituting a macrodomain,

$$P(wx\cdots yz) = (1/n)\sum P(wx\cdots yx)_i. \tag{2}$$

Because these probabilities are independent, and not joint, probabilities, the simplifying assumption of statistical stationarity cannot be employed for the system as a whole, except as noted below.

However, systems that obey low-order Markovian statistics at the microdomain level but not at the macrodomain level have been characterized by equations based on an expansion of Eq. (2). These equations characterize each dyad or triad in terms of two parameters: 1) average mole fraction of either comonomer in the copolymer and 2) variance of composition about its average value [5].

There are two situations where statistical independence does not affect calculations: 1) When a linear relationship exists between independent and dependent variables, or 2) when all microdomains are exactly equivalent.

LINEAR RELATIONSHIP

In general, if and only if two variables are related linearly, the average value of the one can be calculated from the average value of the other regardless of their distribution. That is, if

$$y = f(x) = mx + b, \tag{3a}$$

then

$$\bar{y} = \bar{f}(x) = f(\bar{x}) = m\bar{x} + b. \tag{3b}$$

Reactivity ratios are not only linear functions of copolymer composition; they are constants over the entire range of copolymer compositions. Therefore, reactivity ratios that define a copolymer system's kinetics on a microdomain level are the same as those calculated from the macrodomain properties of coexistent monomer and copolymer compositions.

However, in slurry reaction mixtures, solvent effects caused by monomer concentrations and ratios themselves might cause kinetic differences, so that in some cases calculated reactivity ratios may well even be nonlinear or even nonunique functions of final polymer composition.

In principle, the product of reactivity ratios (r_1r_2) may be calculated from dyad distributions. However, the relationship is nonlinear, and further, the relationship to copolymer composition is also nonlinear. Therefore, (r_1r_2) products calculated from dyads in a nonhomogeneous Markovian system will always be higher than their true values. Ross [5] has shown that

$$(r_1r_2)' = 1 + \frac{X_2}{[m_0(1 - m_0) - X_2]^2}, \tag{4}$$

where m_0 is the average mole fraction of either comonomer in the copolymer and X_2 is the variance in copolymer composition.

It follows that high and variable values of $(r_1r_2)'$ cannot necessarily be ascribed to a failure of the system to follow Markovian statistics, but rather, they can be considered evidence of nonhomogeneity. It also follows that sequence distributions by themselves can be interpreted in at least two ways and, therefore, cannot provide sufficient data to infer unambiguous reaction mechanisms in nonhomogeneous copolymerizations. On the other hand, measurements of coexistent monomer and copolymer compositions will give an average overall mechanism. Fine details may not be discriminated, however. When multiple catalyst types are present, for example, only average, rather than individual, reactivity ratios are obtained. The relationship is derived in the Appendix to Cozewith and Ver Strate's paper [6].

EQUIVALENT MICRODOMAINS

For truly homogeneous copolymerizations, microdomains as here defined, extend in time and space to encompass the entire system. The traditional Markovian approach is valid because

$$(wx\cdots yz) = (wx\cdots yz)_i = (wx\cdots yz)_j. \tag{5}$$

TABLE 2

Polymer	m_0	Sequence distribution (111)	(112)	(212)	(121)	(122)	(222)
A	0.25	0.0156	0.0938	0.1406	0.0469	0.2813	0.4219
B	0.50	0.1250	0.2500	0.1250	0.1250	0.2500	0.1250
C	0.75	0.4219	0.2813	0.0469	0.1406	0.0938	0.0156
D	0.50	0.2188	0.1875	0.0938	0.0938	0.1875	0.2188
E	0.50	0.1875	0.2084	0.1042	0.1042	0.2084	0.1875

But this situation may not ordinarily be assumed. It is incumbent upon the investigator in each case to demonstrate homogeneity before using it to interpret data.

As an example, in a "thought experiment," we may prepare three copolymers (A, B, C above) that exactly follow Markovian statistics. We will also blend equal parts of A and C to form Mixture D and equal parts of A, B, and C to form Mixture E. When sequence distributions are calculated, we find the data presented in Table 2.

We may also calculate the variances ($X_2 = (1/n)\Sigma\delta_i$) as 0.0625 and 0.0416 for Blends D and E, respectively. If Blends D and E are analyzed and treated as experimentally synthesized copolymers, the triad data can be tested against various models as shown in Table 3.

These data reject a zero-order Markovian mechanism and show a reasonable but not exact fit to first-order Markovian. As expected, the nonhomogeneous correlations exactly replicate the data. One might also conclude from the higher than calculated values of triads (111) and (222) that the copolymers tend to be somewhat blocky, or alternatively, nonhomogeneous.

Mixtures of ideal Markovian copolymers do not follow Markovian mathematics in aggregate when nonhomogeneity is present, and as expected, $(r_1r_2)'$ values derived from dyad measurements are greater than unity, as predicted by Eq. (4). Therefore, previous studies that dismiss a low-order Markovian mechanism based directly or indirectly on sequence distributions and simultaneously do not prove homogeneity are subject to reinterpretation.

Several investigators have employed the heterogeneous catalyst system $TiCl_3$·AA-DEAC to produce insoluble or partially insoluble propylene copolymers. Typically, this catalyst produces polymers with M_w/M_n of approximately 6-10 that may be separated into fractions with varying monomer compositions. Failure of these systems

TABLE 3

			Blend D[a]				
Triad	(111)	(112)	(212)	(121)	(221)	(222)	$(r_1 r_2)'$
Experimental	0.219	0.188	0.094	0.094	0.188	0.219	2.78
Markov, zero order	0.125	0.250	0.125	0.125	0.250	0.125	1.00
Markov, first order	0.195	0.234	0.070	0.070	0.234	0.195	2.78
Nonhomogeneous [5]	0.219	0.188	0.094	0.094	0.188	0.219	2.78
			Blend E[b]				
Triad	(111)	(112)	(212)	(121)	(221)	(222)	$(r_1 r_2)'$
Experimental	0.188	0.208	0.104	0.104	0.208	0.188	1.96
Markov, zero order	0.125	0.250	0.125	0.125	0.250	0.125	1.00
Markov, first order	0.170	0.243	0.087	0.087	0.243	0.170	1.96
Nonhomogeneous [5]	0.188	0.208	0.104	0.104	0.208	0.188	1.96

[a] $P(m|r) = P(r|m) = 0.375$, X_2 0.0625.

[b] $P(m|r) = P(r|m) = 0.417$, X_2 0.0416.

to satisfy calculated sequence distributions, as in the example above, may be ascribed to a failure to follow Markovian mechanisms or, alternatively, they may be Bernoullian and nonhomogeneous. Coexistent monomer-copolymer composition data show the overall reaction for these polymers does follow a zero-order Markovian mechanism. Therefore, it is very probable that these polymerizations are in reality nonhomogeneous and Bernoullian.

This analysis also intimates that higher-order Markovian equations are probably as unnecessary in real life as they are cumbersome, especially for Ziegler-Natta-catalyzed system.

CONCLUSIONS

We conclude for nonhomogeneous systems that:

1. Microdomains are statistically independent of each other so that assumptions of statistical stationarity cannot be applied to the polymer as a whole.
2. Because of nonhomogeneity, systems that follow Markovian kinetics within microdomains will not, in general, do so on a macroscale.
3. Sequence distribution data by themselves cannot be used to establish unambiguous reaction mechanisms for nonhomogeneous systems. For these systems, they define the degree of nonhomogeneity present.
4. Coexistent monomer-copolymer compositions by themselves will define an average effective copolymerization mechanism independent of sequence distribution data. These data can demonstrate the reasonableness of nonhomogeneous mechanism.
5. Completely homogeneous reactions are a limiting case of nonhomogeneity ($X_2 = 0$). They may therefore agree with Markovian probabilities on a macroscale if they do so on a microscale.
6. Reported failures of systems to follow lower-order Markovian mechanisms based on distribution data should be reviewed for nonhomogeneity. And as a corollary, complex mathematical models that can never be validated experimentally should only be considered if nonhomogeneity fails as an adequate explanation of the data.

REFERENCES

[1] H. K. Frensdorff and R. Pariser, J. Chem. Phys., 39, 2303 (1963)

[2] G. E. Ham, Copolymerization (High Polymers, Vol. XVIII), Wiley-Interscience, New York, 1964.

[3] M. Kakugo, Y. Naito, K. Mizunuma, and T. Miyatake, Macromolecules, 15, 1150 (1982).

[4] Y. Doi, R. Ohnishi, and K. Soga, Makromol. Chem., Rapid Commun., 4, 169 (1983).
[5] J. F. Ross, J. Macromol. Sci.–Chem., A21, 453 (1984).
[6] C. Cozewith and G. Ver Strate, Macromolecules, 4, 482 (1971).

Received October 29, 1985
Revision received January 9, 1986