Alternating Copolymers

Edited by

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Preface

Examination of the early literature attests to the fact that the study of copolymerization was initiated when polymer science was in its infancy. It has continued to grow to a subject of major importance and has been a source of interest to both academic and industrialist alike. The wide spectrum of structures and properties available in the statistical copolymer has made this a fruitful field of exploration, but one particular and more restricted form which has held its own fascination for many is the limiting case of the strictly alternating copolymer. This is formed, in the ideal situation, when two monomers in a reaction mixture add consecutively to create a polymer chain with a regular ⫫ABABAB⫩ structure, irrespective of the monomer feed ratio. When this happens the resulting copolymer will always have the same composition, a feature which can be advantageous but also somewhat restrictive, as the ability to vary the properties is then limited.

Within a series entitled *Speciality Polymers* it seems appropriate then to deal with this subject, particularly as no previous attempt has been made to draw together the various facets of alternating copolymerization into one volume. It also seems timely to present a more unified picture of the subject which will also illustrate the progress made. The book is not designed to be an exhaustive catalog or a detailed description of every alternating copolymer known, but rather a focusing of attention on what appears to have been a diffuse area of research. Alternating copolymers have often been regarded as mere chemical curiosities, but sufficient work has now appeared to indicate there is more to the subject than that, and this volume may help to strengthen this attitude.

When it was found that alternating structures could be prepared in a reproducible fashion, it was inevitable that an explanation for this unusual behavior would be sought. As this was not immediately forthcoming, a lot of the published work is concerned with this problem. Initially, the effort

was concentrated on systems which either copolymerized spontaneously or were initiated by free radical sources. This is covered in Chapter 2, where the controversial role of the charge-transfer complex in the mechanism of alternation is explored and several systems are examined in detail. The observation that the addition of a Lewis acid to some systems often enhances the alternation has extended this area dramatically. These systems now encompass comonomer combinations which were hitherto unable to produce products with very high degrees of alternation but already showed some tendency to act in this way, and Chapter 3 is devoted to work in these complexed systems. Less common are the systems which use a Ziegler–Natta-type complex as the stimulant for alternation, and in Chapter 4 their influence on olefins and diolefins is discussed. The chemistry of the polymerization methods is rounded off in Chapter 5 by a treatment of the reactions involving zwitterions, which provide very special examples of alternating copolymerizations.

These chapters are most deeply concerned with the mechanism and kinetics of the reactions. The questions of charge transfer complex involvement and the extent of such participation in the formation of alternating structures are recurrent themes. It must never be forgotten, however, that ultimately the properties of the end product are all important, and one must be concerned with potential end uses for such materials. This makes the final chapter particularly relevant as it attempts to summarize the properties of alternating copolymers. It begins by outlining the ways in which the alternating copolymer can be characterized and then proceeds to a description of the various physical properties, after which it tries to put these in perspective and assess the advantages which may accrue from further investigations. While excellent kinetic and mechanistic studies abound, there is a need for much more effort in the area of property evaluation and it is hoped that this volume will highlight this deficiency and serve to stimulate interest in this area in particular and the whole field in general.

J. M. G. Cowie

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Principles of Alternating Copolymerization

J. M. G. Cowie

1. INTRODUCTION

Polymerization reactions involving two or more monomers have been under investigation ever since the systematic study of polymer science began in the 1930s. During that early period it was quickly recognized that copolymerization reactions possessed unique features which distinguished them from homopolymerizations and also made their interpretation more complex. It was observed that the composition of a copolymer could not necessarily be expected to have the same composition as the mole ratio of the monomers in the feed mixture, but that this was more likely to drift as the reaction progressed. Neither was it assured that every pair of monomers would copolymerize effectively, and in some cases actual inhibition of copolymerization by one of the monomers could be observed.

Nevertheless, copolymerizations have continued to evoke interest, and one of the main advantages of the technique is that it provides a convenient method of synthesizing new polymeric structures with a wide range of properties. These can often be closely controlled by making adjustments to the composition and monomer sequences in the chain. That being so, it becomes important to be able to understand what factors influence and control these features; it also becomes necessary to be able to predict the tendency of one monomer to react with another.

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2. MONOMER SEQUENCES

When two monomers M_1 and M_2 are mixed together in the presence of an initiator there are a number of different ways in which the monomers may combine. The final reaction product may be

a. a mixture of homopolymers formed exclusively from either M_1 or M_2;

b. a copolymer containing a statistically random mixture of M_1 and M_2 units in the chain, incorporated in the same proportion as that in the feed;

c. a copolymer in which M_1 and M_2 units alternate in a regular fashion along the chain, e.g., $\sim\sim M_1 M_2 M_1 M_2 M_1 M_2 M_1 M_2 \sim\sim$; or

d. copolymers with structures intermediate to the extreme cases of (b) and (c).

A copolymer with the structure described in (b) is known as an *ideal* copolymer, but is not commonly encountered in practice. The other limiting case is (c), the alternating copolymer, and these two can be represented schematically as in Figure 1, by plotting the % of monomer M_1 in the copolymer (F_1) against its composition in the feed (f_1). Most statistical copolymerizations lead to copolymers with intermediate structures, the compositions of which are determined by the relative reactivities of the two monomers. This is a measure of the tendency of each monomer to enter the chain during the propagation reaction and can be quantified by considering a simple series of reactions for chain propagation by a radical chain carrier. The first attempt to deal with this was made by Dostal,[1] who assumed that the rate of addition of a monomer to a radical is independent of the size and nature of the radical chain and is influenced only by the
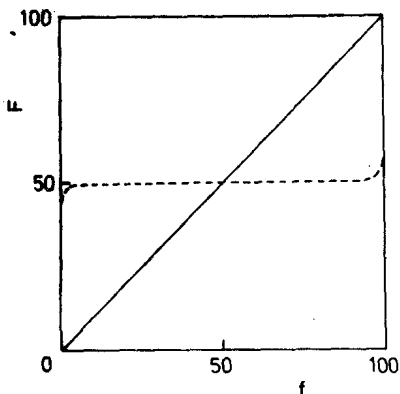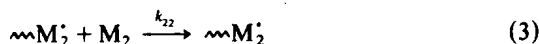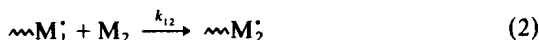

Figure 1. Schematic representation of an ideal copolymerization (solid line) and an alternating copolymerization (broken line).

nature of the radical end group. The four reactions proposed in this classical "terminal" model were as follows:

$$\sim\!\!M_1^{\bullet} + M_1 \xrightarrow{\ k_{11}\ } \sim\!\!M_1^{\bullet} \tag{1}$$

$$\sim\!\!M_1^{\bullet} + M_2 \xrightarrow{\ k_{12}\ } \sim\!\!M_2^{\bullet} \tag{2}$$

$$\sim\!\!M_2^{\bullet} + M_2 \xrightarrow{\ k_{22}\ } \sim\!\!M_2^{\bullet} \tag{3}$$

$$\sim\!\!M_2^{\bullet} + M_1 \xrightarrow{\ k_{21}\ } \sim\!\!M_1^{\bullet} \tag{4}$$
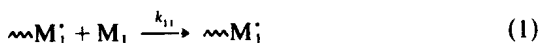
It follows that if the rate constants $k_{12} = k_{11}$ and $k_{21} = k_{22}$ then the frequency of incorporation of either M_1 or M_2 into the copolymer chain will be determined solely by the concentration ratio of the monomers in the feed and an ideal copolymerization will occur [case (b)]. On the other hand, case (a) is obtained if $(k_{12}/k_{11}) = (k_{21}/k_{22}) = 0$ and parallel polymerization of the two monomers takes place. An alternating sequencing of M_1 and M_2 in the chain takes place if k_{12} and k_{21} are very much larger than k_{11} and k_{22}, as then a growing chain terminating in an $M_1^{\bullet}$ radical will add an M_2 unit exclusively and vice versa [case (c)].

It is also important to consider the magnitude of the various rate constants, as high molecular weight alternating structures will form only when k_{12} and k_{21} values are as large as 10^2–10^3 dm^3 mol^{-1} s^{-1}, otherwise only a low molecular weight product is obtained.

Assumption of steady-state conditions[2-5] for the elementary reactions (1)–(4) leads to an equation for instantaneous copolymer composition:

$$\frac{m_1}{m_2} = \frac{[M_1]}{[M_2]}\left(\frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}\right) \tag{5}$$

Here (m_1/m_2) is the instantaneous composition of the copolymer when the composition of the monomers in the reaction mixture is $([M_1]/[M_2])$. The parameters r_1 and r_2 are the monomer reactivity ratios and provide a measure of the preference a radical has for reacting with its own monomer rather than with the comonomer in the mixture, i.e.,

$$r_1 = \frac{k_{11}}{k_{12}} \quad , \quad r_2 = \frac{k_{22}}{k_{21}}$$

Large values of r will then be indicative of a tendency to form long homopolymer sequences, whereas small values of r imply rapid cross propagation reactions and represent a tendency towards alternation.

These reactivity ratios are unique to each comonomer pair and can be used as a guide to the type of copolymer structure which is likely to be formed in the reaction. An ideal copolymer will then be one for which the product $(r_1 r_2) = 1$, while conditions for an alternating system are $(r_1 r_2) \approx 0$. This only provides a crude indication of the structure, which is much more dependent on the actual values of both r_1 and r_2. If both r_1 and r_2 are less than unity it can be said that there will be a tendency for alternating sequences to be formed, but only if $r_1 = r_2 \ll 1$ can regular alternation be expected, i.e. the comonomer pair maleic anhydride $(r_1 \sim 0)$ and styrene $(r_2 \sim 0.0095)$ when mixed with a radical initiator form a highly alternating structure.

The argument can perhaps be more easily understood if the statistical analysis is examined. If P_{11} is the probability that a monomer M_1 will add onto a radical chain terminating in its own species, thereby forming an $\sim\!\!\sim\!\!M_1 M_1^{\cdot}$ sequence, then the addition of another M_1 unit to this growing chain will have a probability $P_{11}{}^2$. The probability of forming a sequence of n of these M_1 units will then be

$$P_{11}^{(n-1)} P_{12} \tag{6}$$

where P_{12} is the probability of also adding an M_2 unit. From a practical viewpoint the individual reaction rates v_{ij} for steps (1)–(4) can be related to the probabilities so that

$$P_{11} = \frac{v_{11}}{v_{11} + v_{12}} = \frac{r_1[M_1]}{r_1[M_1] + [M_2]} \tag{7}$$

$$P_{12} = (1 - P_{11}) = \frac{[M_2]}{r_1[M_1] + [M_2]} \tag{8}$$

$$P_{22} = \frac{v_{22}}{v_{22} + v_{21}} = \frac{r_2[M_2]}{r_2[M_2] + [M_1]} \tag{9}$$

$$P_{21} = (1 - P_{22}) = \frac{[M_1]}{r_2[M_2] + [M_1]} \tag{10}$$

This analysis shows that in a system with $r_1 = r_2 = 0.1$, the chains formed will have, on average, nine alternating $[M_1 - M_2]$ sequences for every one nonalternating $[M_1 - M_1]$ or $[M_2 - M_2]$ sequence. If $r_1 = r_2 = 0.01$ then there are 99 alternating sequences for every one nonalternating diad. Consequently conditions for a strictly alternating copolymer must be $r_1 = r_2 = 0$ and $(m_1/m_2) = 1$.

3. MONOMER REACTIVITY

An examination of the many systems which have been studied has revealed that cross-propagation reactions are not favored when the monomer pairs have different reactivities. Random copolymers tend to form most easily when the comonomers are similar as reactive species, but it has become apparent that the relative reactivities are controlled by two factors, resonance stabilization and polarity.

3.1. Resonance Stabilization

In an extensive study of copolymerizing systems, Mayo and his co-workers[6-8] noted that certain monomer pairs exhibited a tendency to alternate, which resulted from either steric effects or differences in the electron donor–acceptor properties of the radical and the double bond of the incoming monomer. Generally speaking, it was found that an unstable radical will favor reaction with a resonance stabilized monomer rather than with an unstable monomer, and that a resonance stabilized terminal radical prefers to add an unstable monomer. They also observed that the rate of addition of a monomer is higher if it forms a resonance-stabilized radical from a non-resonance-stabilized monomer, than the opposite. Thus in the styrene (1)-vinyl acetate(2) system, $r_1 = (k_{11}/k_{12}) = (176/3.2) = 55$, which shows that styrene monomer adds onto its own resonance stabilized radical 55 times faster than vinyl acetate monomer (stable) can add to the styrene radical. However, $r_2 = (k_{22}/k_{21}) = 3.7 \times 10^3/3.7 \times 10^5) = 10^{-2}$, and this indicates that the addition of styrene monomer to the vinyl acetate radical is 100 times faster than the addition of the vinyl acetate monomer. The result is that the copolymerization is very poor for this pair of monomers.

3.2. Polarity

Alternating effects cannot be explained satisfactorily by differences in resonance stabilization, and instead we must also consider the polarity of the double bond as a factor influencing the formation of this regular structure. A monomer such as acrylonitrile may be represented as a partially polarized structure:

$$CH_2\!\!=\!\!CH\overset{\delta+}{-}C\overset{\delta-}{\equiv}N$$
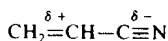
and if a similar polarization occurs in the radical then this monomer will prefer to add onto a chain, terminating in a radical unit with an electron

donating substituent, if available, e.g.,

$$CH_2{=}CH{-}\langle\ \rangle^{\delta+}$$
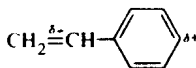
rather than to its own radical. Consequently alternation is enhanced by marked differences in the polarity of the double bond and is most obvious when a powerful electron donor–acceptor comonomer pair are involved in the copolymerization.

4. THE $Q{-}e$ SCHEME

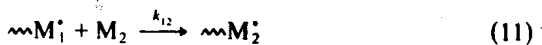Most copolymerization reactions will be influenced by both polar and resonance stabilization effects but to different extents, and in an attempt to quantify this Alfrey and Price[9] developed the "$Q{-}e$" scheme. For the cross-propagation reaction

$$\sim\!\!M_1^{\bullet} + M_2 \xrightarrow{\ k_{12}\ } \sim\!\!M_2^{\bullet} \tag{11}$$

the relation they suggested was

$$k_{12} = P_1 Q_2 \exp\left(-e_1 e_2\right) \tag{12}$$

where P characterizes the radical state and Q is a measure of the monomer reactivity, and e_1 and e_2 describe the polarization characteristics of the radical and the reacting monomer, respectively. It was further assumed that the polarization of a radical and its monomer were indistinguishable. A standard was selected to which all other monomers could be related, and styrene, with $Q = 1$ and $e = -0.8$, was selected for this purpose. A series of values can then be established for other monomers and a representative sample can be found in Table 1. A more comprehensive list is available in the *Polymer Handbook*.[10]

The scheme provides only a qualitative guide to the copolymerization behavior of pairs of monomers; those with similar Q and e values will tend to undergo ideal polymerization, whereas the formation of alternating copolymers is favored when the Q values are similar, but more importantly when the e values are high and of opposite sign. For example, maleic anhydride ($Q = 0.23$; $e = +2.25$) tends to form alternating copolymers with monomers such as butadiene ($Q = 2.39$; $e = -1.05$) and α-methyl styrene ($Q = 0.98$; $e = -1.27$).

TABLE 1
Q and *e* Values for Selected Monomers

Monomers	Q	e
Acrylamide	1.120	1.19
Acrylic anhydride	1.270	0.51
Acrylonitrile	0.600	1.20
1,3-Butadiene	2.390	−1.05
iso Butylene	0.033	−0.96
iso Butyl vinyl ether	0.023	−1.77
Carbon monoxide	0.100	3.76
p-Cyanostyrene	1.610	0.30
Cyclohexene	0.002	−1.44
Ethylene	0.015	−0.20
Fumaronitrile	0.800	1.96
Indene	0.360	−1.03
Isoprene	3.330	−1.22
Maleic anhydride	0.230	2.25
Methyl acrylate	0.420	0.60
Methyl methacrylate	0.740	0.40
α-Methylstyrene	0.980	−1.27
Methyl vinyl ketone	1.000	0.70
Methyl vinyl sulfide	0.320	−1.45
2-Methylene glutaronitrile	0.570	1.11
Propylene	0.002	−0.78
Styrene	1.000	−0.80
Tetrachloroethylene	0.003	2.03
Vinyl acetate	0.026	−0.25
Vinyl chloride	0.044	0.20

The alternating tendency can then be expressed as a product of the two monomer reactivity ratios:

$$(r_1 r_2) = \exp\left[-(e_1 - e_2)^2\right] \tag{13}$$

and this is consistent with the suggestion that $(r_1 r_2) \approx 0$ will represent an alternating system.

Attempts have been made to improve the $Q-e$ scheme,[11] in which the fraction of alternating diads $(F_{12} + F_{21})$ in the system was used to measure the degree of alternation. The modified expression was

$$(F_{12} + F_{21}) = \frac{2}{2 + (r_1 + r_2)([M_1]/[M_2])} \tag{14}$$

but the approach still remains qualitative at best. Some evidence of a