

Copolymerization

Toward a Systematic Approach

Cornel Hagiopol

Copolymerization

Toward a Systematic Approach

Cornel Hagiopol

*Lehigh University
Bethlehem, Pennsylvania*



Kluwer Academic / Plenum Publishers
New York, Boston, Dordrecht, London, Moscow

Hagiopol, Cornel.

Copolymerization: toward a systematic approach/Cornel Hagiopol.

p. cm.

Includes bibliographic references and index.

ISBN 0-306-46179-X

1. Polymerization. 2. Copolymers. I. Title.

QD281.P6H24 1999

547'.28—dc21

99-42892

CIP

The PROCOP (version 2.3) and sample files on the CD-ROM found inside the back cover are covered by the following statement:

Copyright © 1999 by Octavian Frangu and Cornel Hagiopol.

The computer code and or data in this file is provided for demonstration purposes only with no guarantee or warranty of any kind that it is correct or produces correct results. By using the code and or data in this file the user agrees to accept all risks and liabilities associated with the code and or data. The computer code and or data in this file may be copied (and used) for noncommercial academic or research purposes only, provided that this notice is included. This file or any portion of it may not be resold, rented, or distributed without the written permission of the author.

A PC and Windows 98® are required to read or use the CD-ROM.

The files are organized in one directory: PROCOP. To start the program click on the **PROCOP.exe** file on the appended CD-ROM. For details on using the CD-ROM, please refer to the User Guide.

For further information, contact the authors via e-mail at ofran@pcnet.ro or hagiopol@aol.com

ISBN 0-306-46179-X

©1999 Kluwer Academic/Plenum Publishers, New York

233 Spring Street, New York, N.Y. 10013

<http://www.plenum.com>

10 9 8 7 6 5 4 3 2 1

All rights reserved

No part of this book may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, microfilming, recording, or otherwise, without written permission from the Publisher

Printed in the United States of America

FOREWORD

With the millennium approaching, it is interesting to look back at the last one hundred years and reflect on the degree to which science and technology have changed our lives. We have experienced an explosive growth in technology and are astonished at how transportation progressed from the horse and buggy to air travel; likewise, we advanced in computational power to the present computer age. On a numerical scale, the horse and buggy could travel perhaps six miles per hour and the jet plane six hundred miles per hour, representing an increase in the speed of travel of two orders of magnitude. Computationally we have gone from one arithmetic operation per second to desktop computers capable of doing over one thousand computations per second. While going from horse and buggy travel to jet planes is certainly impressive, the growth in computational power is spectacular.

Polymers had a similar burst of growth. There was no man-made polymer production at the turn of the century. While the scale of change in polymer production is similar to the computer industry, the observable effects on our every day life is more subtle, but equally significant. Polymers are present at every turn, for example in wall paint and in the paper coating on which we write. Most commercial polymers comprise two or more monomers, which were carefully engineered for a particular end use application. It is surprising with the rapid growth in polymer production that no comprehensive discussion about all the significant advances in co-polymerization exists.

Copolymerization: Toward a Systematic Approach is an excellent resource in fulfilling that need and is kinetically oriented with significant attention given to the treatment of reaction rate constants for both binary and ternary systems. A number of coordinated computer programs that allow the calculation or estimation of the reaction rate constants are available on the included disk. This is further combined with statistical analysis of the data giving confidence intervals for the reactivity ratios and calculated polymer compositions from feed composition data. This is of particular significance, since every one who has practiced the design of co-polymers or the designing of reactors for co-polymer manufacture, has found a wide spread of data for reactivity ratios or reaction rate constants. Invariably, for critical work

the reaction rate constants must be measured for the specific system. This applies to all modes of free radical polymerization, from bulk to emulsion and suspension polymerization. This book is of particular use for those who have the need to extract the 'most likely' reaction rate parameters from experimental data. Beside end-use engineering and reactor design and modeling, accurate reaction rate constants are needed for rigorous engineering calculations, as in heat transfer and agitation scale-up. The publication of this book gives a critical review of all previous, significant work with functional computer programs that are easy to use.

Andrew Klein
Lehigh University
Chemical Engineering Department
and Emulsion Polymers Institute
Bethlehem, PA

PREFACE

Copolymerization is one of the most dynamic areas of polymer science. The number of copolymers obtained exceeds by far that of homopolymers. The study of copolymers has opened or further expanded commercial fields one could have hardly imagined 50 years ago. Copolymerization has become a very widely used industrial process, and new copolymers are constantly being created. Given this impressive growth rate, macromolecular chemistry has gradually turned into copolymer chemistry. Homopolymerization can be regarded as a particular case of copolymerization when the initial feed composition of the second comonomer is set to zero. The interest shown by scientists all over the world in copolymerization-related issues is illustrated by the great number of articles dealing with copolymerization and copolymers; in addition, major contributions have been worldwide, coming from teams of researchers associated with, among others, the University of Waterloo in Canada, Eindhoven University of Technology in The Netherlands, Lehigh University in the United States, the University of Pais Vasco in Spain and the University of Queensland in Australia.

Following the development of the composition equation in 1944 (Mayo, Lewis, Wall, Alfrey, and Goldfinger), it was till possible over the next two decades for the literature to keep pace with the rapidly evolving experimental material (e.g., Mayo and Walling, 1950; Alfrey, Bohrer, and Mark, 1952; Young, 1961; Ham, 1964 references will be cited in the subsequent chapters). In the past few decades, however, the accumulation of experimental data has defied attempts at systematic treatment. Moreover, in the remarkable effort to find new materials a wide gap has emerged between theoretical rigor and experimental procedure. Thus, there are far too many uncertain, sometimes even contradictory results. The fitting of experimental results in a consistent framework is, if not impossible, very hard to achieve, particularly because of the divergent approaches to conducting copolymerization experiments. Optimum experimental design (Tidwell and Mortimer, 1965) has rarely been used.

This book attempts to identify the basic elements of most papers published in this field and to filter them through a consistent evaluation strategy. Particular

attention is given to two elements of the composition equation: real values of reactivity ratios (for binary and ternary copolymerization) and actual comonomer concentrations (for solution, emulsion, and suspension copolymerization). The quality and effectiveness of experimental programs is also discussed.

This book treats the definition of various kinetic models, their estimation through different calculation methods, the discrimination among kinetic models by means of composition data, and the influence of the reaction environment upon the values of reactivity ratios. Both binary and ternary copolymerization processes are considered.

Special attention is given to identifying factors that can compromise the reliability of the values recorded for reactivity ratios. A reassessment of the published experimental data is performed for each of the cases under study.

To facilitate calculations, computer programs devoted to copolymerization-related issues were developed by Octavian Frangu, and are appended to this book. They are particularly helpful for finding solutions to problems raised by the use of composition equations, estimating copolymer composition according to monomer composition (for a chosen kinetic model of binary or ternary copolymerization), integrating composition equations up to high conversions, fitting approximate 95% confidence intervals, applying differential and integral calculation methods for reactivity ratios, and calculating azeotrope compositions, among other things.

The present book and accompanying diskette present a strategy which should allow polymer chemists to evaluate experimental data on a common basis. It is my hope that future research will fill in current gaps in this field and that copolymerization will gradually become a more consistently structured area of study. For this reason this book is basically a monograph complemented by a practical guide toward a systematic approach.

To exploit fully the constantly increasing amount of experimental data, this information will have to be appropriately assessed and applied for an understanding of the copolymerization process. This is one of the aims of the present book.

Without attempting to provide a new way of thinking about copolymerization per se, this book does suggest a new way to understand it.

"Copolymerization" is an arrow pointed toward the future.

CONTENTS

1. Binary Copolymerization

1.1. Copolymers and Copolymerization Processes	1
1.2. The Terminal Kinetic Model: The Copolymer Composition Equation	3
1.3. Copolymerization Reaction Types	7
1.4. The Integral Form of the Copolymerization Equation	9
1.5. Use of the Differential and Integral Forms of the Mayo–Lewis Equation to Describe Copolymerization Processes	10
1.5.1. Composition Curves for Copolymerization Processes . . .	10
1.5.2. Composition versus Conversion Curves	13

2. Estimation of Reactivity Ratios

2.1. Analysis of Experimental Data	19
2.2. How Consistent Are Existing Reactivity Ratios?	22
2.3. Differential Methods for Calculating Reactivity Ratios	25
2.3.1. Linear Methods	27
2.3.2. Nonlinear Methods	47
2.4. Preliminary Remarks on an Experimental Strategy for Estimating Reactivity Ratios	57
2.5. Shortcomings of Differential Methods when Conversion Is Taken into Account	60
2.6. Estimation of Reactivity Ratios when Conversion Values Are Taken into Account	64
2.6.1. The Extended Kelen–Tüdös Method	65
2.6.2. The Kuo–Chen Method	66
2.6.3. The Mao–Huglin Method	67
2.6.4. The Intersection Method	67
2.6.5. The Optimization Method	69
2.6.6. The Error-in-Variables Method	73

2.7. The Use of Composition versus Conversion Data in Estimating Reactivity Ratios	74
2.8. Recalculated Values for Reactivity Ratios	76
2.9. Experimental Errors and Effectiveness of the $Q-e$ Scheme	95
3. Ternary Copolymerization	
3.1. The Terminal Kinetic Model: The Alfrey–Goldfinger Equation . .	101
3.1.1. Variation of Ternary Copolymer Composition as a Function of Initial Feed Composition	103
3.1.2. Change of Ternary Copolymer Composition as a Function of the Conversion Level	104
3.1.3. Restricted Forms of the Composition Equation	106
3.2. Estimation of Reactivity Ratios Directly from Ternary Copolymerization Data	110
3.3. Azeotropy with Ternary Copolymerization	115
3.3.1. Unitary Azeotropes	116
3.3.2. Binary Azeotropes	118
3.3.3. Ternary Azeotropes	119
3.4. Consistency of Reactivity Ratio Values Used in Ternary Copolymerization	120
3.5. Do Ternary Azeotropes Exist? (Pseudoazeotropy)	126
4. Going Beyond the Limits of the Terminal Model	
4.1. The Extent to Which the Mayo–Lewis Equation Can Fit All Copolymerization Data	131
4.2. Higher Order Kinetic Models	137
4.2.1. Kinetic Model Including Effects of the Penultimate Unit	137
4.2.2. Kinetic Model Including Effects of the Antepenultimate Unit	140
4.2.3. Model Including Participation of a Charge Transfer Complex	142
4.2.4. Estimation of Reactivity Ratios for Higher Order Models	146
4.3. The Potential of Experimental Composition Data	148
4.4. Optimal Experimental Design for Estimating Reactivity Ratios	153
4.5. Model Discrimination	155
4.5.1. Case of a Comonomer Which Does Not Homopolymerize	157
4.5.2. The Case when $r_i, r_j \neq 0$	166
4.6. Generalized Kinetic Model for Binary Copolymerization	170

5. Homogeneous and Heterogeneous Copolymerization

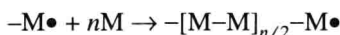
- 5.1. Copolymerization within Initially Homogeneous Systems 182
- 5.2. Emulsion Copolymerization 192
- 5.3. Copolymer Composition and the Mechanism of Emulsion
Copolymerization 197

6. Running a Copolymerization Process 207**Bibliography 209****Index 227**

BINARY COPOLYMERIZATION

1.1. COPOLYMERS AND COPOLYMERIZATION PROCESSES

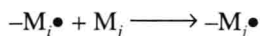
A macromolecular chain is created by homopolymer synthesis during the so-called propagation step. This is the stage where the greatest amount of monomer is consumed and the highest number of chemical bonds (M–M) is formed:



where $-M\bullet$ is the free macroradical and n is the average degree of polymerization.

It is quite simple to identify the structural unit, as the composition is constant along the macromolecular chain. Polydispersity will only arise from differences in length of the polymer molecules. It is thus possible to predict the polymer properties (physical and mechanical properties, interactions with solvents or with other macromolecular compounds, etc.) as a function of the monomer structure, the average molecular weight, and the molecular weight distribution.

Binary copolymerization represents a disturbance of the homopolymerization process via the introduction of a second monomer (M_2). A significant change occurs in the propagation step, which now includes homopolymerization of comonomers as well as cross-propagation;



where $i \neq j$. Thus the generation of $-M_i-M_j-$ bonds becomes possible, providing the difference between a homopolymer and a copolymer.

Binary copolymerization is defined by the inclusion within a copolymer of two comonomers. With a higher number of comonomers, copolymerization becomes multicomponent.

The copolymer structure depends at every moment of the reaction on (among other things) the relative comonomer concentrations and on their reactivity (polarity, resonance, and steric factors). The conversion factor is also very important.

Copolymers have a chemical composition distribution that depends on the molecular weight distribution. Accordingly, the compositional distribution differs

from one molecule to another and there is also a variation of the copolymer composition along the macromolecular chain.¹⁻⁴

With regard to comonomer reactivity, the copolymer structure will depend on the propagation mechanism.⁵ The present book is devoted to the study of free-radical copolymerization.

From the viewpoint of chain architecture, copolymers can be classified into four types: statistical, alternating, block, and graft. This classification is based upon the distribution of both M_i-M_j and M_i-M_i bonds,^{1,2} and is described as follows:

- (a) For *statistical copolymers* the distribution of M_j in a hypothetical chain of M_i is of statistical type.
- (b) For *alternating copolymers* the macromolecule is formed by the rigorous succession $-M_i-M_j-M_i-M_j-$. It is highly improbable to be able to identify the characteristic structure of the homopropagation step ($-M_i-M_i-$ or $-M_j-M_j-$) with these copolymers.
- (c) For *block copolymers* the number of $-M_i-M_i-$ bonds (which form the homopolymer sequences called "blocks") exceeds by far the number of bonds generated through cross-propagation. Diblock copolymers exhibit just one $-M_i-M_j-$ bond.
- (d) *Graft copolymers* exhibit one backbone and several branches. Depending on the structure of their backbones and branches, several categories of graft copolymers can be identified: homopolymer-statistical copolymers, statistical, alternating, or block-type copolymers-statistical copolymers, etc.

The wide diversity in the chemical structures of copolymers is obvious. Thus, it is quite difficult to define the structural unit that might repeat itself along the copolymer macromolecule. Dyads ($-M_i-M_j-$, $-M_i-M_i-$ and $-M_j-M_j-$) and triads (M_i -centered triads: $-M_i-M_i-M_i-$, $-M_j-M_i-M_i-$ and $-M_j-M_i-M_j-$) can be identified.

When the distribution of comonomer units in a copolymer structure is of the statistical type one finds a composition distribution as well as a molecular weight distribution. The composition distribution is of two types: within the macromolecule (all along it) and between different macromolecules generated (for instance) at various moments during copolymerization.

It is obvious that the number of copolymers exceeds by far that of homopolymers. Compared to the number of homopolymers, the number of copolymers is practically infinite (binary, ternary, grafted copolymers with various comonomer ratios).

It is very difficult to identify the properties of a copolymer from the architecture of the macromolecule. Of prime importance for the structure-properties relationship is the compositional heterogeneity.¹ One practically has to deal with an infinite field of research and the potential generation of spectacular new materials. A huge amount of surprise awaits the researcher.

The diverse succession of chemical bonds mostly results in unexpected copolymer properties which are not simply the arithmetic average of the corresponding mixture of homopolymers, and one should not expect a linear variation of properties as a function of composition.

Quite frequently copolymer properties are determined not only by the overall composition, but also by the distribution of the chemical composition.^{1,6} Incorporating a small amount of other structural units through copolymerization can modify the miscibility behavior of a polymer. Guiding both global and composition distributions is the main target of the researcher in copolymerization. The present book is devoted to help that researcher (or student) better understand issues of copolymer synthesis. It is the possibility of generating compounds of highly complex structure that has led to exceptional properties (in the sense of exceptions from the so-called rules) and has resulted in the convulsive and paradoxical history of copolymerization research.

The activity in the field seems to be divided between experimental work and efforts to model and deepen theoretically the study of the processes involved. Up to now, experiment-oriented researchers have definitely been winning the battle with those who have tried to set rules governing these processes and to predict their development.

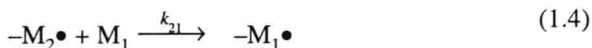
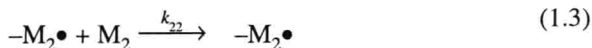
This book deals in part with the need to redefine experimental strategies.

1.2. THE TERMINAL KINETIC MODEL: THE COPOLYMER COMPOSITION EQUATION

In 1944 equations governing the relationship between the comonomer composition and the copolymer composition were found through three independent developments.⁷⁻⁹ These attempts to organize and improve the processing of experimental data have significantly contributed to copolymerization research, as shown by a comparison between the number and style of articles published before and after the studies of Mayo and Lewis, Alfrey and Goldfinger, and Wall.

Mayo and Lewis introduced the first kinetic model of free-radical copolymerization, the so-called terminal kinetic model. The equation was established in relation to the propagation step (the stages where the most significant comonomer consumption occurs) and it accounted for the contribution of four separate reaction possibilities in copolymerization:





where the k_{ij} are propagation rate coefficients.

The development of the copolymerization equation involved the following assumptions:

1. One is dealing with a chain reaction involving long chains, so that the consumption of monomer and the copolymer composition can be discussed solely in terms of chain propagation reactions. A negligible amount of monomer is consumed by reactions with free radicals arising from the decomposition of a free-radical initiator and from the chain-transfer reaction to initiator, solvent, or copolymer. This assumption has been mathematically verified.¹⁰ A strong chain transfer to one of the comonomers¹¹ is taken into account when the molecular weight is small (3000).¹² Maleic anhydride-furan copolymers contain up to 6% initiator fragments.
2. The free macroradicals have very short lives compared to the length of the overall reaction so that steady-state expressions can be set up for the concentrations of active centers.
3. The last-added monomer unit only affects the reactivity of free macroradicals. It is assumed that the specific reaction rate constants are unaffected by polymer chain length.
4. Possible interactions between comonomers, or between comonomers and solvent, are not taken into account.

Under these conditions, the rate of disappearance of the two monomers is given by

$$-\frac{dM_1}{dt} = k_{11}[M_1\bullet][M_1] + k_{21}[M_2\bullet][M_1] \quad (1.5)$$

$$-\frac{dM_2}{dt} = k_{22}[M_2\bullet][M_2] + k_{12}[M_1\bullet][M_2] \quad (1.6)$$

where k_{ii} is the rate constant for the individual polymerization step and $-M_i\bullet$ represents the growing free radicals.

If equation (1.5) is divided by equation (1.6), we obtain

$$\frac{dM_1}{dM_2} = \frac{k_{11}[M_1\bullet][M_1] + k_{21}[M_2\bullet][M_1]}{k_{22}[M_2\bullet][M_2] + k_{12}[M_1\bullet][M_2]} \quad (1.7)$$

and the concentrations of free macroradicals are eliminated by combining equation (1.7) with the equation (1.8), which gives the steady-state expression.

$$k_{12}[M_1\bullet][M_2] = k_{21}[M_2\bullet][M_1] \quad (1.8)$$

The final copolymerization equation is

$$\frac{dM_1}{dM_2} = \frac{m_1}{m_2} = \frac{M_1}{M_2} \frac{r_1 M_1 + M_2}{M_1 + r_2 M_2} \quad (1.9)$$

where m_1 and m_2 are the mole fractions of the copolymerized monomers, M_1 and M_2 are the mole fractions of unpolymerized comonomers, and r_1 and r_2 are defined as:

$$r_1 = \frac{k_{11}}{k_{12}}, \quad r_2 = \frac{k_{22}}{k_{21}} \quad (1.10)$$

Equation (1.9) is a relationship between the overall copolymer composition and the composition of the monomer mixture and the reactivity ratios r_i of the comonomers. The reactivity ratios are effectively constant, independent of feed monomer composition, and are characteristic of each comonomer pair under study.

The term dM_1/dM_2 stands for the instantaneous composition of the copolymer resulting from the instantaneous comonomer feed composition (M_{i0}). Accordingly, the copolymer composition is usually different from the comonomer feed composition. That is why changes in comonomer and copolymer compositions occur during copolymerization processes. Copolymerization is a kinetically controlled process, and equation (1.9) is of a differential type.

If the comonomer consumption in the initiation and termination steps is taken into account, a similar, but more sophisticated equation is obtained.¹³

In spite of the fact that other, more sophisticated and more complete equations were proposed,¹⁴ equation (1.9) became the most frequently used relationship in macromolecular chemistry. Its use represented a turning point in defining and estimating monomer reactivity ratios. All articles published since have taken into account the form of the equation and have aimed at determining reactivity ratios via specific methods. To this end, authors have adopted the strategy of carefully selecting the comonomer ratio and using a large number of experiments with a view to increasing confidence in the values of the reactivity ratios.

The simplicity of equation (1.9) has accounted for its huge success. Even if some reservations can be expressed with regard to it, we can confidently say that its assumptions seem to be correct since the mathematical model based on these assumptions with appropriate values of r_1 and r_2 appears to fit the data.

The essential correctness of the Mayo–Lewis equation has been experimentally checked in a large number of cases. The limitations of the equation are dealt with in Chapter 4.

Equation (1.9) has been further used even with copolymerization processes that involve multifunctional comonomers.^{15–17} For two double-bond monomers the following equation was proposed:

$$\frac{dM_1}{dM_2} = \frac{2M_1}{M_2} \left(\frac{2r_1M_1 + M_2}{2M_1 + r_2M_2} \right) \quad (1.11)$$

As the copolymerization is kinetically controlled, one ought to look at propagation constants. The expression for the average propagation rate coefficient, k_p ,¹⁸ is

$$k_p = \frac{r_1M_{10}^2 + 2M_{10}M_{20} + r_2M_{20}^2}{r_1M_{10}/k_{11} + r_2M_{20}/k_{22}} \quad (1.12)$$

This already points to a fundamental characteristic of copolymerization processes: the rate will change with changes in the comonomer ratio, and with the conversion, which is a very important consideration.

The terminal model has generally been found to describe adequately copolymer composition and has failed in only a small number. This, however, is not the case for the overall rate of propagation, which generally shows deviations from the predictions of the terminal model and uses monomer reactivity ratios obtained from composition data.

The copolymer structure is used to determine reactivity ratios and is involved in evaluating the validity of the terminal model. This accounts for the importance of the relationship between the copolymer structure and the reactivity ratios.

The following equations^{19–21} indicate the probability of 1–2, 2–1, and 1–1 bond generation, respectively:

$$P_{1-2} = \frac{M_{20}}{M_{20} + r_1M_{10}} = \frac{T_{121} + T_{122}/2}{T_{121} + T_{122} + T_{222}} \quad (1.13)$$

$$P_{2-1} = \frac{M_{10}}{M_{10} + r_2M_{20}} = \frac{T_{212} + T_{112}/2}{T_{111} + T_{112} + T_{212}} \quad (1.14)$$

$$P_{1-1} = \frac{M_{10}}{M_{10} + r_1M_{20}} \quad (1.15)$$

where the T_{iji} represent M_j -monomer-centered triads.

The number-average sequence length,²⁰ as the reciprocal of the conditional probability, can be expressed as²²

$$\begin{aligned}\overline{N}_1 &= r_1 \frac{M_{10}}{M_{20}} + 1 \\ \overline{N}_2 &= r_2 \frac{M_{20}}{M_{10}} + 1\end{aligned}\quad (1.16)$$

The average number of monomer sequences occurring per 100 monomer units (run number) can also be used to characterize the sequence distribution. The run number²³ can be related to any measurable feature (including copolymer composition) that depends on the sequence distribution.

The terminal model predictions for M_1 -monomer-centered triads²⁴ are given by

$$T_{111} = \frac{r_1^2 [M_1]^2}{r_1^2 [M_1]^2 + 2r_1 [M_1][M_2] + [M_2]^2} \quad (1.17)$$

$$T_{211} = T_{112} = \frac{r_1 [M_1][M_2]}{r_1^2 [M_1]^2 + 2r_1 [M_1][M_2] + [M_2]^2} \quad (1.18)$$

$$T_{212} = \frac{[M_2]^2}{r_1^2 [M_1]^2 + 2r_1 [M_1][M_2] + [M_2]^2} \quad (1.19)$$

The expressions for M_2 -centered triads can be obtained by switching subscripts 1 and 2 in the above equations. As with composition data, triad fractions depend only on monomer feed compositions and reactivity ratios.

All the above relations involve reactivity ratios. Thus the values of the reactivity ratios need to be determined very accurately.

The increase in the number of comonomers for which data are tabulated is an illustration of the effort made in this field over the past five decades.²⁵⁻²⁹ The reactivity ratios have been studied and listed for a very large number of copolymerization systems. Effort has also been made to increase the reliability of these values by processing previous experimental data with improved calculation methods.^{30,31} Accordingly, a huge amount of experimental data is available, and will be assessed in this book using criteria that will be given in subsequent chapters.

1.3. COPOLYMERIZATION REACTION TYPES

Instantaneous copolymer compositions are functions of reactivity ratios and monomer feed compositions.

Examination of hundreds of copolymer systems over the years has shown that a substantial proportion exhibit preferential reaction between free radical and unlike monomer for $r_1 < 1.0$ and/or $r_2 < 1.0$.