POLYMER MOLECULAR WEIGHTS

(in two parts)

PART I

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MARCEL DEKKER, INC. New York

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270 Madison Avenue, New York, New York 10016

LIBRARY OF CONGRESS CATALOG CARD NUMBER: 74-80625

ISBN: 0-8247-6227-4

Current printing (last digit):

10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

Chapter 1
INTRODUCTION

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Macromolecules have many of the characteristics of simple molecules; that is, most will dissolve in common solvents, they exhibit colligative properties, have chemically reactive functional groups, and absorb energy at specific wavelengths. One problem unique to polymers, however, is that the molecules may be composed of varying amounts of smaller monomer units. These changes in the degree of polymerization result in molecules with differing molecular weights and, indeed, in differing distributions of those molecular weights. Polymeric materials with molecular weights ranging from a few hundred to several million are not uncommon, even within the same population group made in the same reaction vessel at the same time. This infamous phenomenon has initiated many hours of research and is the reason that this book exists.

The determination of polymer molecular weights can become a difficult task for the novice in polymer physical chemistry. The actual laboratory experimentation is not complex in most cases, but the treatment of the data can be very involved. Fortunately, the use of electronic computers has resolved this problem to some extent. However, many laboratories are not blessed with this aid nor with competent programers to insert the proper numbers in the correct sequence. In order to make the best use of the data that we obtain from the laboratory by any of the techniques discussed in later chapters, we must understand the basic concepts of polymer molecular weight and how to calculate the numbers we use. It is hoped that this book will help clarify unanswered questions and resolve some of the difficulties in measuring this macromolecular parameter.

I. MOLECULAR WEIGHT AVERAGES

Extreme care must be exercised when molecular weight terminology is used since several systems for expressing this information exist. Different types of experimental procedures will yield data that vary widely, since they will measure completely independent properties. Accordingly, molecular weight averages must be defined to accomodate the particular data considered. The most commonly used terms describing the experimental data are number average molecular weight, M_n; viscosity average molecular weight, M_v; weight average molecular weight, M_w; the "Z-average," M_z and "Z + 1 average," M_{z+1}. Each of these will be considered for their meaning and interelationships.

A. Number Average Molecular Weight

If a technique for molecular weight determination is selected that is dependent on the number of molecules present, that is, colligative properties, the function obtained is the number average molecular weight. Examples of these techniques are membrane osmometry, boiling point elevation, and end group analyses. All colligative property measurements depend on the mole fraction of solute present, N_2, assuming that the concentration of the solute is small enough that Henry's law is obeyed. Polymers, however, have a number of different species of solute dissolved in this dilute solution, since we have a distribution in the degree of polymerization, and each of these species will be present at its own concentration. It is thus necessary to add all of these mole fractions together to determine the total solute mole fraction.

To accomplish this, we first total the number of moles $\sum_i N_i$ of solute present. Here N_i is the number of moles of solute of species i. Likewise, the total weight of the sample, W, is

$$W = \sum_i W_i \tag{1-1}$$

where W_i is the actual weight in grams of species i. Since moles times molecular weight is equal to weight in grams, we may also write

$$W = \sum_i N_i M_i \tag{1-2}$$

The number average molecular weight, M_n, is now defined as the total weight of all solute species, divided by the total number of moles present. Thus

$$M_n = W/\sum_i N_i \tag{1-3}$$

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