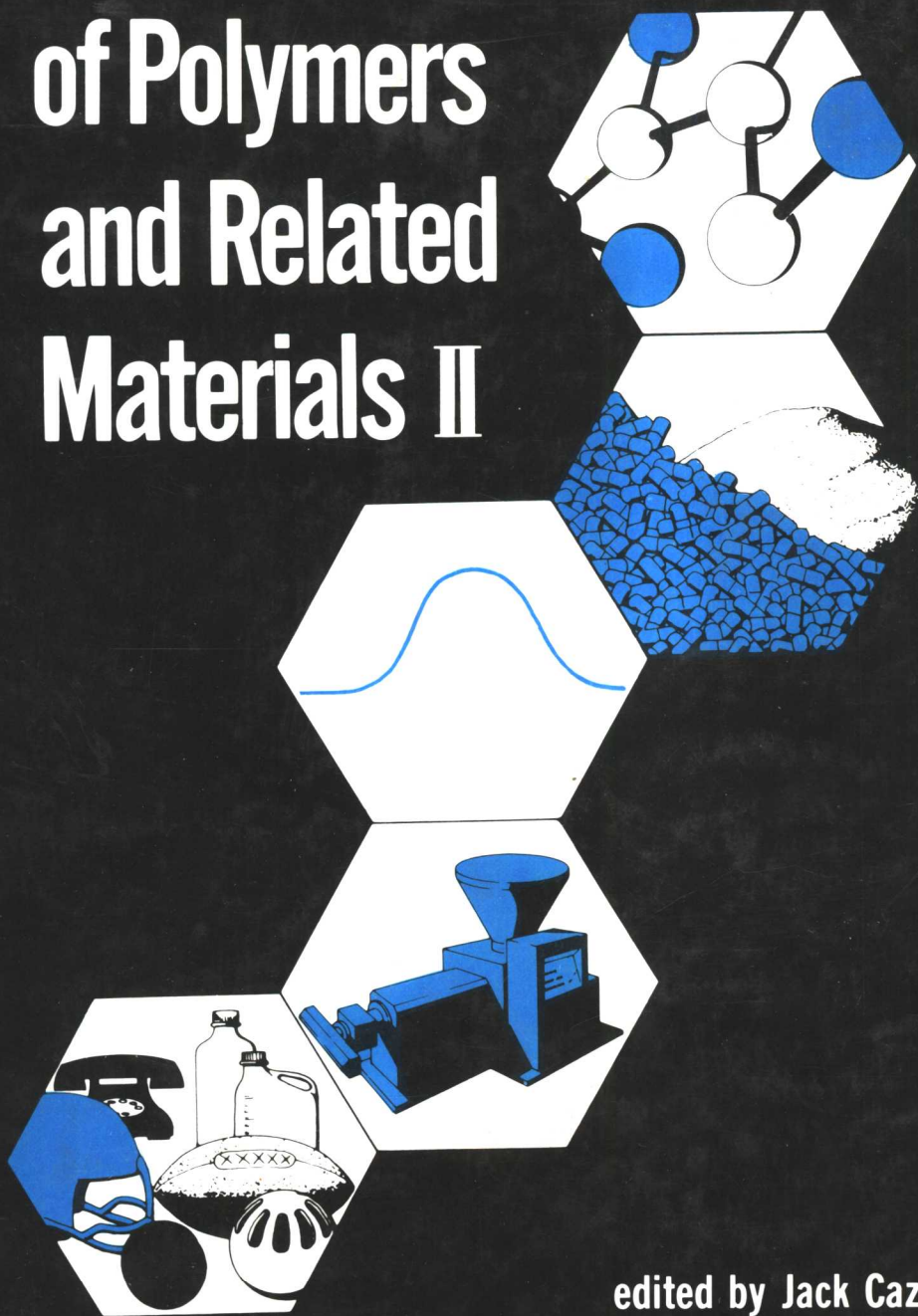


CHROMATOGRAPHIC SCIENCE SERIES

VOLUME 13

Liquid Chromatography of Polymers and Related Materials II



edited by Jack Cazes
and Xavier Delamare

Liquid Chromatography of Polymers and Related Materials II

edited by

JACK CAZES

Waters Associates, Inc.
Milford, Massachusetts

and

XAVIER DELAMARE

Waters Associates, Inc.
Paris, France

MARCEL DEKKER, INC. New York and Basel

Library of Congress Cataloging in Publication Data

International Liquid Chromatography Symposium,
Palais des congres et de la musique, 1979.
Liquid chromatography of polymers and related
materials II.

(Chromatographic science ; v. 13)

Includes indexes.

1. Polymers and polymerization--Analysis--
Congresses. 2. Liquid chromatography--Congresses.

I. Cazes, Jack

II. Delamare, Xavier

III. Title.

QD139.P6155 1979

547.8'4046

80-16061

ISBN 0-8247-6985-6

COPYRIGHT © 1980 by MARCEL DEKKER, INC. ALL RIGHTS RESERVED

Neither this book nor any part may be reproduced or transmitted in
any form or by any means, electronic or mechanical, including photo-
copying, microfilming, and recording, or by any information storage
and retrieval system, without permission in writing from the publisher.

MARCEL DEKKER, INC.

270 Madison Avenue, New York, New York 10016

Current printing (last digit):

10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

CHROMATOGRAPHIC SCIENCE

A Series of Monographs

Editor: JACK CAZES

*Waters Associates, Inc.
Milford, Massachusetts*

- Volume 1: Dynamics of Chromatography
J. Calvin Giddings
- Volume 2: Gas Chromatographic Analysis of Drugs and Pesticides
Benjamin J. Gudzinowicz
- Volume 3: Principles of Adsorption Chromatography: The Separation of Nonionic Organic Compounds
Lloyd R. Snyder
- Volume 4: Multicomponent Chromatography: Theory of Interference
Friedrich Helfferich and Gerhard Klein
- Volume 5: Quantitative Analysis by Gas Chromatography
Josef Novák
- Volume 6: High-Speed Liquid Chromatography
Peter M. Rajcsanyi and Elisabeth Rajcsanyi
- Volume 7: Fundamentals of Integrated GC-MS (in three parts)
Benjamin J. Gudzinowicz, Michael J. Gudzinowicz, and Horace F. Martin
- Volume 8: Liquid Chromatography of Polymers and Related Materials
Jack Cazes
- Volume 9: GLC and HPLC Determination of Therapeutic Agents (in three parts)
Part 1 edited by Kiyoshi Tsuji and Walter Morozowich
Parts 2 and 3 edited by Kiyoshi Tsuji
- Volume 10: Biological/Biomedical Applications of Liquid Chromatography
Edited by Gerald L. Hawk
- Volume 11: Chromatography in Petroleum Analysis
Edited by Klaus H. Altgelt and T. H. Gow
- Volume 12: Biological/Biomedical Applications of Liquid Chromatography II
Edited by Gerald L. Hawk
- Volume 13: Liquid Chromatography of Polymers and Related Materials II
Edited by Jack Cazes and Xavier Delamare

Other Volumes in Preparation

PREFACE

Published in this volume are selected papers presented at the Fourth International Liquid Chromatography Symposium: Liquid Chromatography of Polymers and Related Materials, which was held on October 24-25, 1979 at the Palais des Congres et de la Musique, Strasbourg, France. Included are thirteen papers covering a range of topics of interest to those involved in the fractionation and characterization of polymeric substances.

We thank the authors of these contributed papers for the fine work they have done and reported here, and also for their patience in the preparation of their manuscripts.

Special thanks are extended to Mrs. Cecile Daly for her valuable assistance, patience, and understanding at all stages of the preparation of this volume.

Lastly, thanks to Waters Associates, Inc., for sponsoring the symposium and for making their facilities available during the preparation of the final manuscript.

Jack Cazes
Xavier Delamare

CONTRIBUTORS

- K.B. ABBAS, Telefonaktiebolaget LM Ericsson, Stockholm, Sweden
- S. ARRIGHETTI, Assoreni, Polymer Research Laboratories, San Donato, Milan, Italy
- A.M. BASEDOW, Universitat Heidelberg, Heidelberg, Federal Republic of Germany
- R. BRESSAU, BASF Aktiengesellschaft, Kunststofflaboratorium, Ludwigshafen, am Rhein
- B. BRULÉ, Laboratoire Central des Ponts et Chaussees, Paris Cedex, France
- M. BRUZZONE, Assoreni, Polymer Research Laboratories, San Donato, Milan, Italy
- A. CAMPOS, Universidad de Bilbao, Bilbao, Spain
- A.F. CUNNINGHAM, Materials Quality Assurance Directorate, Royal Arsenal East, Woolwich, United Kingdom
- J.V. DAWKINS, Loughborough University of Technology, Loughborough, Leicestershire, England
- A. DE CHIRICO, Assoreni, Polymer Research Laboratories, San Donato, Milan, Italy
- K.H. EBERT, Universitat Heidelberg, Heidelberg, Federal Republic of Germany

- J.E. FIGUERUELO, Universidad de Valencia, Burjasot (Valencia), Spain
- G.N. FOSTER, Union Carbide Corporation, Bound Brook, New Jersey
- Z. GALLOT, Centre de Recherches sur les Macromolecules, CNRS, Strasbourg, France
- D.J. GOEDHART, Akzo Corporate Research Arnhem, Arnhem, Velperweg 76, The Netherlands
- A.E. HAMIELEC, McMaster University, Hamilton, Ontario, Canada
- C. HEATHCOTE, Materials Quality Assurance Directorate, Royal Arsenal East, Woolwich, United Kingdom
- D.E. HILLMAN, Materials Quality Assurance Directorate, Royal Arsenal East, Woolwich, United Kingdom
- J.B. HUSSEM, Akzo Corporate Research Arnhem, Arnhem, Velperweg 76, The Netherlands
- J. LESEC, Laboratoire de Physico-Chimie des Polymers, Paris, France
- T.B. MAC RURY, Union Carbide Corporate, South Charleston, West Virginia
- J.I. PAUL, Materials Quality Assurance Directorate, Royal Arsenal East, Woolwich, United Kingdom
- J.P.M. ROELS, The State University of Leiden, Leiden, The Netherlands
- B.P.M. SMEETS, Akzo Corporate Research Arnhem, Arnhem, Velperweg, The Netherlands
- J.A.M. SMIT, The State University of Leiden, Leiden, The Netherlands
- V. SORIA, Universidad de Valencia, Burjasot (Valencia), Spain
- J.A.P.P. VAN DIJK, The State University of Leiden, Leiden, The Netherlands

CONTENTS

Preface	iii
Contributors	vii
Problems Encountered in the Determination of Average Molecular Weights by GPC Viscometry	1
J. Lesec	
High Performance Gel Permeation Chromatography of Polymers	19
J.V. Dawkins	
Investigations Concerning the Mechanism of GPC	41
A.M. Basedow and K.H. Ebert	
Polymer Retention Mechanisms in GPC on Active Gels	49
J.E. Figueruelo, V. Soria and A. Campos	
Problems in Multiple Detection of GPC Eluents	73
R. Bressau	
Aqueous Gel Permeation Chromatography: The Separation of Neutral Polymers on Silicagel	95
J.A.P.P. van Dijk, J.P.M. Roels and J.A.M. Smit	
Utilization of Multidetector System for Gel Permeation Chromatography	113
Z. Gallot	

Molecular Characterization of Degraded Polymers	123
K.B. Abbas	
Characterization of Polymers with Long Chain Branching- Development of the Molecular Weight and Branching Distribution (MWBD) Method	143
G.N. Foster, T.B. MacRury and A.E. Hamielec	
Gel Permeation Chromatography of Nitrocellulose	173
A.F. Cunningham, C. Heathcote, D.E. Hillman and J.I. Paul	
GPC and Viscometric Investigations on Grafting Reaction of SAN onto EPM Elastomer	197
A. DeChirico, S. Arrighetti and M. Bruzzone	
GPC of Polyamides	203
D.J. Goedhart, J.B. Hussem and B.P.M. Smeets	
Contribution of Gel Permeation Chromatography (GPC) to the Characterization of Asphalts	215
B. Brulé	
Author Index	249
Subject Index	257

PROBLEMS ENCOUNTERED IN THE DETERMINATION OF AVERAGE
MOLECULAR WEIGHTS BY GPC VISCOMETRY

J. Lesec

Laboratoire de Physico-Chimie des Polymeres
Paris, France

ABSTRACT

This paper deals with problems that are encountered in modern GPC with dual detection (refractometer-viscometer) when calculating average molecular weights, that can lead to incorrect values. Three main problems are developed: axial dispersion in columns, dependence of elution volumes upon solute concentration, and application of the hydrodynamic volume concept. In each case, we have tried to emphasize the best method that takes into account these different effects, avoiding data treatment errors and that leads, thus, to the best accuracy in the determination of average molecular weights of polymers.

INTRODUCTION

Gel Permeation Chromatography is a modern method of polymer characterization which can be used in two different ways. One can only try to obtain a representation of the polymer molecular distribution. The GPC chromatogram is then directly recorded to compare polymers with different molecular distributions. Calculations can then be performed on the chromatographic data to determine average molecular weight values. In this case, GPC can be considered as a real measurement system which is going to take the place of traditional methods of average molecular weight determination and, consequently, as with every technique leading to numerical evaluation of physical values, must withstand a critical analysis. For this

reason, it seems important to take stock of the measurement method's validity and the accuracy that we can expect from calculations performed with chromatographic data.

We will consider the situation where only the steric exclusion process arises without perturbing phenomena such as adsorption or partition whose effects were recently described⁽¹⁾, and we will discuss the different errors that can affect molecular weight values given by GPC. We can thus classify two kinds of errors⁽²⁾:

- typical chromatographic errors
- data treatment errors.

Typical chromatographic errors are directly related to instrumentation and chemicals. They can lead to very wrong molecular weight values when a chromatographic analysis is not performed under very well defined conditions. The main reasons are: the molecular weight accuracy of standards used for calibration, the problem of sample dissolution, the determination of exact elution volumes in relation to the mobile phase flow rate stability, the accuracy of the substance amount which is injected into the column set and peak shifts resulting from solute concentration and column temperature effects.

But we will assume here that our chromatographic instrumentation is perfect and we will only examine the problems encountered in GPC data treatment when calculating polymer average molecular weights: correction of solute concentration, correction of axial dispersion and application of universal calibration. We will consider only modern GPC using microgels whose analysis time is about 20 minutes.

PRINCIPLE OF AVERAGE MOLECULAR WEIGHT DETERMINATION

Macromolecular compounds are mainly characterized by a molecular distribution function which depends upon the synthesis process. Therefore, their physical and mechanical properties are directly related to this distribution which can be described by average molecular weight: \bar{M}_n , \bar{M}_v , \bar{M}_w , \bar{M}_z . These molecular weights are usually determined by classical methods (osmometry, viscometry, light scat-

tering, and ultra-centrifugation). But GPC is the only method which can simultaneously lead to all of these parameters. The principle of chromatogram analysis⁽³⁾ is represented in Figure 1. It consists in digitizing the refractometric peak into equal fractions, located at the elution volume V_i and whose surfaces are is proportional to solute concentration C_i . The calibration equation $\text{Log } M_i = f(V_i)$ gives the relation between M_i and V_i ; therefore, summation throughout the peak leads to the average molecular weights.

$$\bar{M}_n = \frac{\sum C_i}{\sum \frac{C_i}{M_i}}, \quad \bar{M}_v = \left(\frac{\sum C_i M_i^\alpha}{\sum C_i} \right)^{1/\alpha}, \quad \bar{M}_w = \frac{\sum C_i M_i}{\sum \frac{C_i}{M_i}}, \quad \bar{M}_z = \frac{\sum C_i M_i^2}{\sum \frac{C_i}{M_i}}$$

But, if universal calibration⁽⁴⁾ $\text{Log } [\eta]_i \cdot M_i = f(V_i)$ is used, we have to simultaneously analyse a second chromatogram, given by a viscometric detector⁽⁵⁻⁷⁾. In addition, molecular weight distribution curves can be plotted⁽⁸⁾, since the relative ratio of each species M_i can be calculated.

In actual fact, the principle of calculation is less evident than it appears. The chromatogram is a very distorted representation of the molecular weight distribution because of the logarithmic nature of the elution⁽⁹⁻¹⁰⁾. If $C(M)$ and $W(V)$, respectively, represent the real distribution and the experimental chromatogram, we can represent the total weight of solute by:

$$\int_{M_1}^{M_2} C(M) \cdot dM = \int_{V_1}^{V_2} W(V) \cdot dV \quad (1)$$

Considering the general equation of a calibration curve:

$$V = F(M) \quad (2)$$

$$\text{and its derivative: } F'(M) = \frac{dV}{dM} \quad (3)$$

by using (2) and (3), (1) becomes:

$$\int_{V_1}^{V_2} \frac{C(M)}{F'(M)} \cdot dV = \int_{V_1}^{V_2} W(V) \cdot dV \quad (4)$$

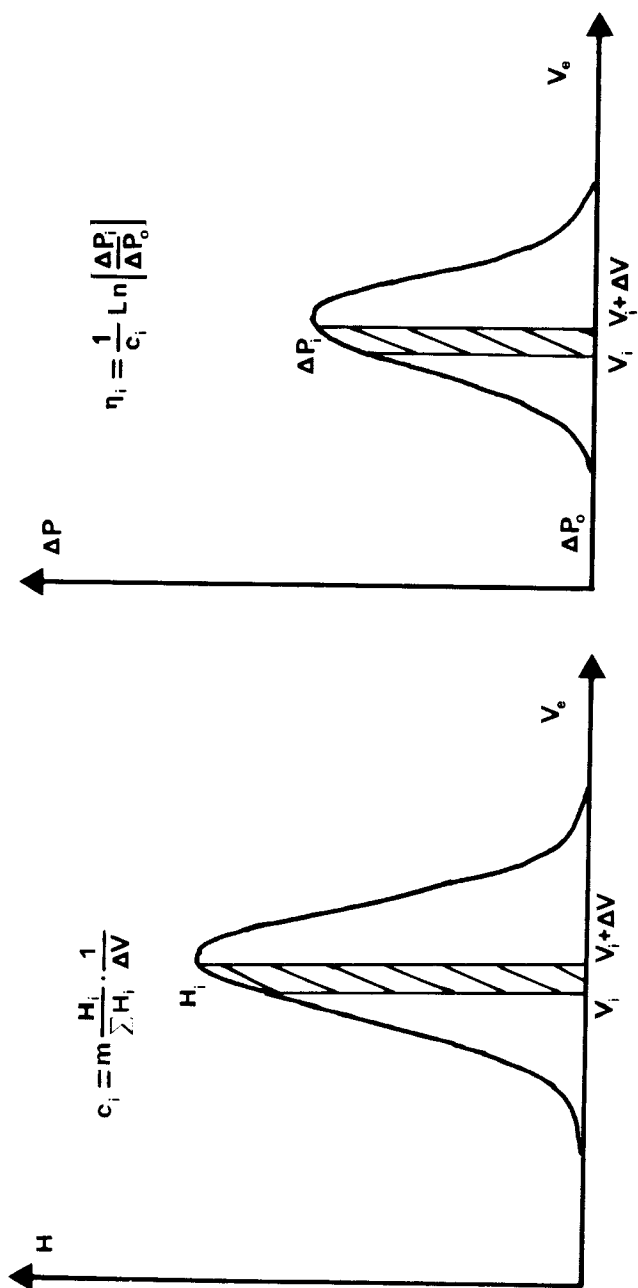


FIGURE 1
Principle of Calculation in Double Detection GPC. (Refractometer-Viscometer). m is the Weight of Solute.

The relationship (4) being true whatever the limits we obtain:

$$C(M) = W(V) \cdot F'(M) \quad (5)$$

In GPC, the logarithmic nature of the elution leads to:

$$W_i(V) = M_i C_i(M) \cdot \frac{1}{\text{Log}_e} \cdot \frac{d\text{Log}M}{dV} \quad (6)$$

Relationship (6) represents the polymer distribution deformation by the GPC phenomenon and gives a correspondance, point by point, between the chromatogram and the real distribution and, consequently, allows its determination⁽¹¹⁾.

Fortunately, in the calculation of molecular weights, this deformation is balanced by the detection system which analyses equal volumes. For example, by using (3) and (5), we can write:

$$\int M \cdot C(M) \cdot dM = \int M \cdot F'(M) \cdot W(V) \cdot dM = \int M \cdot W(V) \cdot dV \quad (7)$$

and carrying (1) and (7) in the definition of \bar{M}_w , we see that:

$$\bar{M}_w = \frac{\int M \cdot C(M) \cdot dM}{\int C(M) \cdot dM} = \frac{\int M \cdot W(V) \cdot dV}{\int W(V) \cdot dV}$$

The same holds true for \bar{M}_n , \bar{M}_v , and \bar{M}_z . This very interesting result points out that we can calculate an average molecular weight by two different ways, both of which lead to an identical result: either by digitizing in dM the real distribution $C(M)$ or by using directly the chromatogram $W(V)$ digitized in dV , whatever the calibration curve. This demonstration makes the correction of calibration curve slope, included in some authors' calculation methods, not justified.

In fact, the simple method described previously can only be strictly applied with an infinite resolution column set, since molecules M_i , eluted at the elution volume V_i , are contaminated by their neighbors (M_{i-1} , M_{i+1} , M_{i-2} , M_{i+2} , etc...) that have diffused in the mobile phase. This is an axial dispersion phenomenon.

THE AXIAL DISPERSION PHENOMENON

Axial dispersion depends upon the column set efficiency. An abundant literature has been devoted to this effect when column efficiencies are poor. With modern columns, axial dispersion is

less important, and we can hope that it will become negligible in the near future. Tung⁽¹²⁾ showed that the experimental chromatogram $F(V)$ and the ideal chromatogram $W(V)$ are linked by the general relationship:

$$F(V) = \int_{-\infty}^{+\infty} W(y) \cdot G(v - y) \cdot dy \quad (8)$$

where $G(v - y)$ is the axial dispersion function, which is generally assumed to be gaussian⁽¹³⁾. Many solutions were proposed to resolve Equation 8: Fourier transform⁽¹⁴⁾, polynomial methods^(12,15), and minimisation method⁽¹⁶⁾. These methods are not easy to apply and generally require involved computation treatments.

A simple method was recently developed by Marais⁽¹⁷⁾. Assuming a gaussian dispersion function, Equation 8 becomes:

$$F(V_e) = \int_{-\infty}^{+\infty} W(V) \cdot \exp - \frac{(V - V_e)^2}{2 \sigma^2} \cdot dV \quad (9)$$

where V_e is the elution volume of the peak apex and σ the axial dispersion parameter of the gaussian dispersion function. A sophisticated resolution of (9) leads to the simple result:

$$\bar{M}_{\beta i} = M_i \left[\exp \frac{\beta \tau^2}{2} \right] \cdot \left[1 + \tau^2 \frac{C'}{C} \right] \quad (10)$$

($\bar{M}_{\beta i} = M_{ni}$ for $\beta = -1$, \bar{M}_{vi} for $\beta = \alpha$, \bar{M}_{wi} for $\beta = 1$) where $\tau = \sigma/a$ (a = slope of the calibration curve), C the distribution curve and C' its derivative. As ratio C'/C is unknown, it can be approximately expressed through H'/H , ratio of the experimental chromatogram derivative on itself:

$$\frac{C'}{C} \approx \frac{H'}{H} \cdot a \quad (11)$$

Relationship 10 permits the calculation of average molecular weights when the parameter τ is determined throughout the chromatogram. The calibration of the parameter σ can be performed by the Waters' recycle method⁽¹⁸⁾ (Fig. 2) which leads to the precise determination of the polydispersity of the polystyrene standards used⁽¹⁹⁾. We could thus obtain⁽²⁾ (Fig. 3) a calibration of τ for a

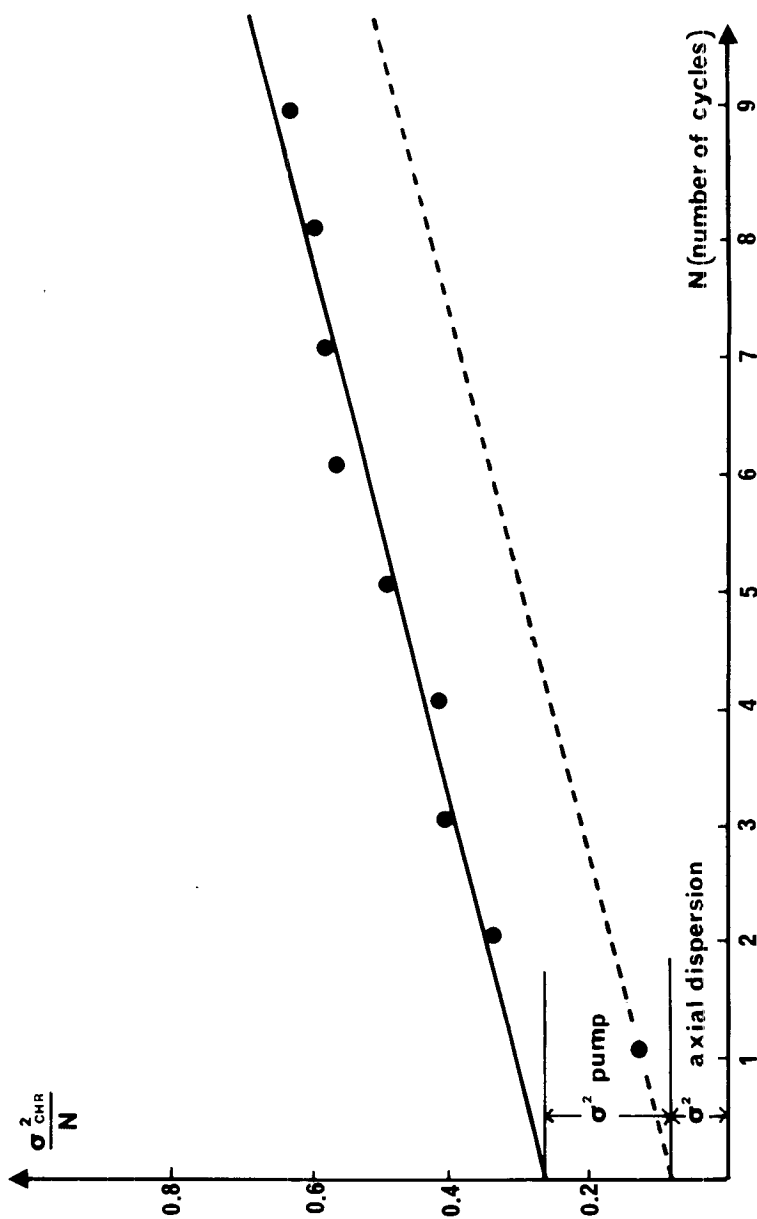


FIGURE 2
Recycling Method of Column Axial Dispersion Calibration and Absolute
Polydispersity Determination (Polystyrene Standard 20,500).

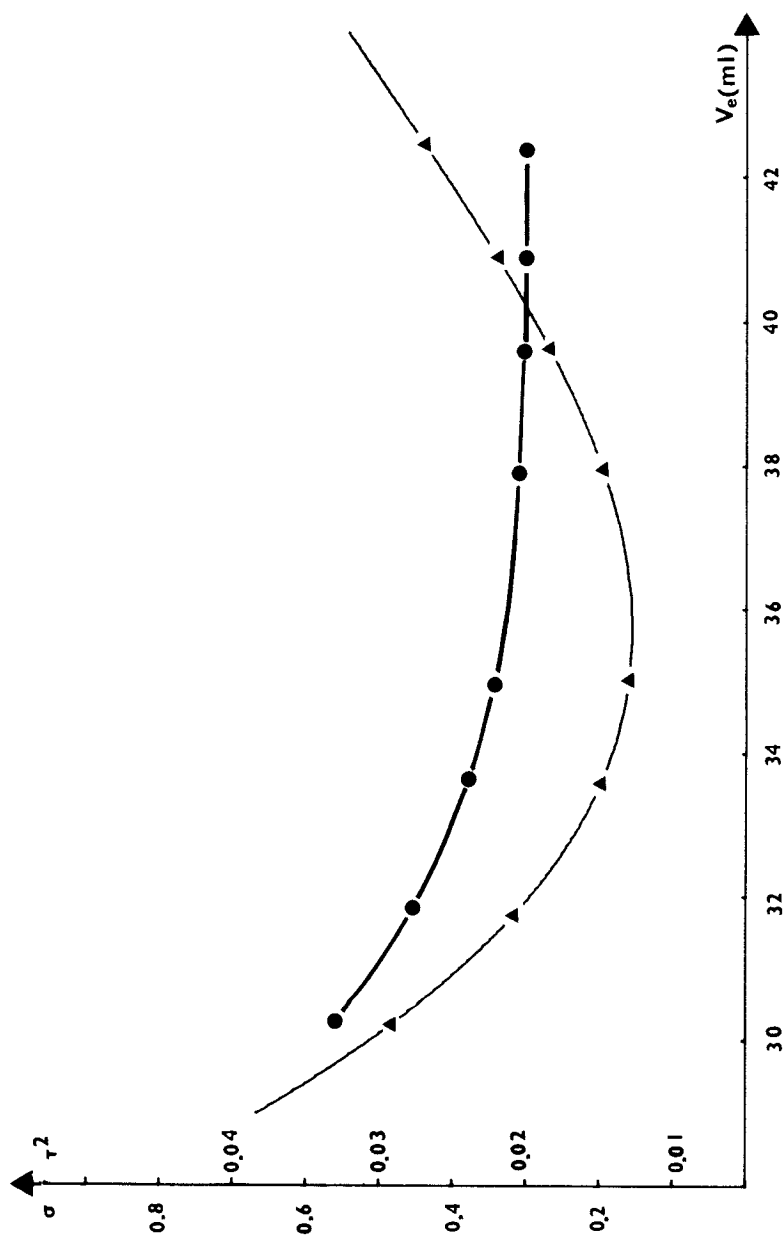


FIGURE 3
Variations of Axial Dispersion Parameters as a Function of Elution Volume:

● $\sigma = f(V)$; ▲ $\tau^2 = \frac{\sigma^2}{2} = f(V)$

μ Styragel 10^3 Å, 10^4 Å, 10^5 Å, 10^6 Å - THF 2 ml/min $\theta = 30^\circ\text{C}$