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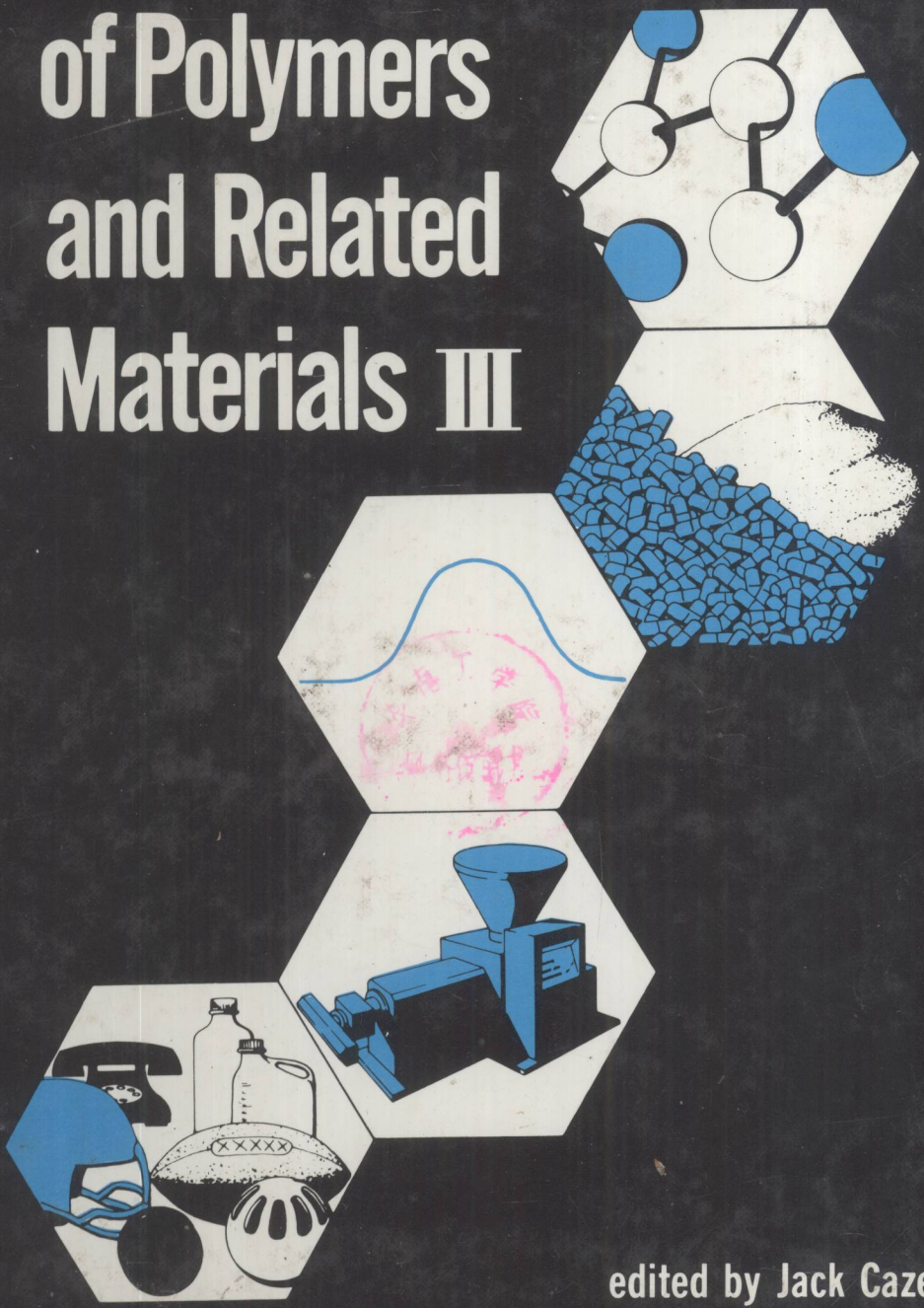
Liquid Chromatography of Polymers and Related Materials III



edited by Jack Cazes

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PREFACE

Published in this volume are papers presented at the International GPC Symposium/80: GPC/LC Analysis of Polymers and Related Materials, which was held on October 23-24, 1980 at the Sheraton Tara Hotel in Framingham, Massachusetts. This volume, the third of a series,* describes new GPC/LC applications and techniques that will provide polymer scientists and practitioners with insight into the development of new polymers and plastics and improvement of existing materials.

I thank the authors of the 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. Nancy Leutert for her valuable assistance in the preparation of the indexes for 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

*The first two volumes of this series are: Liquid Chromatography of Polymers and Related Materials (J. Cazes, ed.), Marcel Dekker, New York, 1977; and Liquid Chromatography of Polymers and Related Materials II (J. Cazes and X. Delamare, eds.), Marcel Dekker, New York, 1980.

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GEL PERMEATION CHROMATOGRAPHY: A TWENTY YEAR VIEW

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ABSTRACT

Reviewing the earlier years of GPC, a few subjects seemed to be unfinished business, and these are discussed. The inception of GPC is cited as an example of the value of a strong driving force and a diverse background in innovation. In support of Casassa's early view of the separation mechanism in GPC, a detailed picture is offered of the internal pore structure of Haller's porous glass. An average pore diameter of 2400 A is found for a glass which showed 1800 by mercury penetration. This brings theory and experiment much closer together. Also, the effects of diffusional non-equilibrium are discussed in their contribution to zone-broadening rather than to earlier elution.

I. INTRODUCTION

For me this fall of 1980 is the twentieth birthday of gel permeation chromatography--GPC. There are still a few things about it that to me are unfinished business and so I would like to get some remarks into the record. First I would like to comment a bit further on my experience at the start of GPC, as an example of the value of a strong driving force and a diverse background in innovation, and

*Now retired.

then I will go on to some aspects of the mechanism of the separation. I do have a little data to present, but mostly I want to give you my picture of what is going on in those little porous beads, for whatever it may be worth to you.

II. HISTORICAL

I have already told about the inception of GPC [1], but there is a story behind that. In 1960 I had been looking closely at liquid chromatography as a research area. Having been involved with development in gas chromatography for several years I thought that continuous operation with high performance columns and plumbing should be made generally available in LC. At that time, much of LC was geared to packing a fresh column for each sample to achieve reproducible adsorption. Column efficiency was rarely noted but it was low, around 150 plates per foot, and it got lower as column diameter increased. The cause was uneven packing and the effect was called channelling. Before GPC could come out that had to be dealt with too. Then one day I ran across the report of Porath and Flodin on Gel Filtration [2]. They had a short broad bed in a Buchner funnel; proteins were excluded from crosslinked dextran particles while salts were delayed by their admission to the gel particles. This was not the first time that molecular size exclusion had come to my attention, but this time I was open for a new project, and things came together. From long association with the manufacture and uses of ion exchange resins, the GC and LC exposures, and a deeply felt need for a good method of getting molecular weight distributions, the vision of GPC took shape rather quickly.

This deeply felt need seems to have been the crucial factor in getting my attention on my opportunity. It arose in the early 1940's when I was developing some polypropylene glycols. Ionically catalyzed, of relatively low molecular weight, their distribution was a clean, narrow Poisson function but we couldn't prove it then. This was painful because our salesmen were sending notes like "this customer was told by our competitor's man that our product doesn't have

a good molecular weight distribution." I was sure he was bluffing, but I didn't know how to handle it. The situation passed quickly but the remembrance did not. After this, anything on molecular weight distribution seemed to catch my attention. I believe this was the subconscious flag that waved when the GPC idea was ready to come forth. This was the source of energy that powered my initial exploration, these polyglycols were in fact my first samples, and my program to tailor-make a series of column packings with the complete range of permeabilities was started when I found the pores of the standard ion-exchange beads were all too small and those of the large-pore beads were too large for those polyglycols. It was also apparent then that we needed much smaller beads with more pore volume and more rigidity, and the means for these were available. Being aware, then, of the widespread availability of these ingredients in my vision of GPC, I thought it very possible that others might have had similar experiences and might even then be working along the same lines. We later found that we were probably no more than a year ahead of others in the basic idea, so my sense of urgency was justified. But it is pleasant to recall that in a year and a half from starting work to first public announcement [3] the basic details of the instrument and its utility were soundly established.

III. SEPARATION MECHANISM - EQUILIBRIUM

Now let us turn to the separation mechanism in gel permeation chromatography. In 1966 I presented some data on columns packed with a very uniform pore glass, kindly made available to me by Dr. Haller at the National Bureau of Standards [4]. The data showed that we were getting some penetration by pretty large molecules, compared to the pore size found by Haller with mercury intrusion, and I suggested that the whole range of conformational sizes of a macromolecule might be involved in its GPC "size" [5,6]. Haller had established that the rigid rods of tobacco mosaic virus were

excluded completely from glass pores much larger than the rod's diameter, but much less than its length. So we had the picture that the molecule's tumbling was faster than its translational diffusion, and that was faster than the change in domain size of a flexible macromolecule. Dr. Ed Casassa at Mellon Institute then took the case of equilibrium in a theta solvent, and calculated the pore penetration of a random coil molecule as that fraction of all its conformations that would not touch the wall of the pore [7]. Dr. Turner Alfrey at Dow had also made such a calculation using a different mathematical treatment but coming to the same conclusion [8]. The pore penetration I reported fitted well with their calculations for a slab-shaped pore of the diameter found by mercury intrusion, but was too great for a tubular pore of that diameter. Please note here that the meaning of K_d, the volumetric distribution coefficient, is here defined implicitly as the ratio of a solute's concentration in the pore to that outside the pore. We will come back to this later.

Now I will offer a correction to the pore diameter we cited then. When a scanning electron microscope (SEM) became available to us, I took the matter up again. We made a number of specimens by potting several grains of Haller's 1800 Angstrom pore glass in gelatin capsules with styrene containing 25 percent divinylbenzene. After opening with a microtome, we used reagent hydrofluoric acid to eat away the glass and expose the pore structure. After washing, mounting and gold-flashing they were examined under the SEM. First we found that an hour or two of etching was nowhere near enough, it took twenty-four hours to stabilize and clear the picture. Then at 30,000 times magnification in an 8 x 10 inch print we had a remarkably clear picture of the pore structure (Fig. 1). Since the pores were formed by the nucleation and growth of a soluble phase in a plastic mass, with coalescing of nuclei, we should expect a recurrent pore diameter, with enlargements, branchings and joinings. I picked out on the print over a hundred of these rather uniform necks at random, measured them, ranked and plotted the measurements at five percent intervals on a linear vs probability basis, shown in Figure 2. They fitted well on a straight line, with mean neck

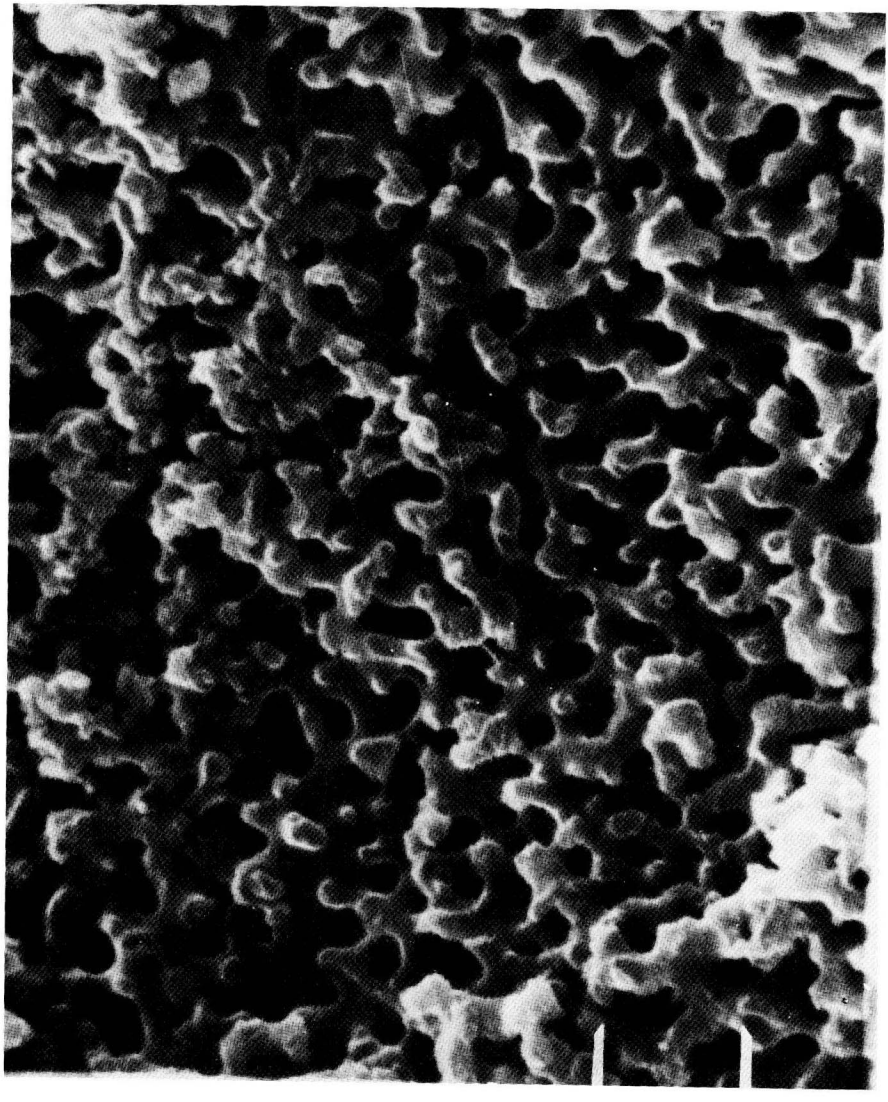

FIGURE 1. Scanning electron micrograph of the pore system of Haller's 1800 Angstrom pore glass, potted in styrene + 25% divinylbenzene, with glass removed. Between points = 1 micrometer.

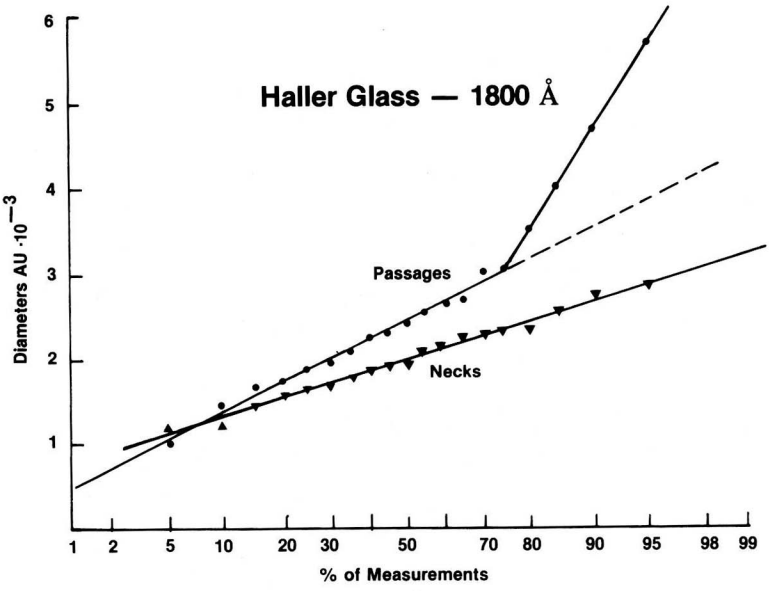

FIGURE 2. Pore diameters in thousands of Angstroms vs percent of measurements, from specimen as above.

diameter of 1970 Å, standard deviation 530 Å. From this picture we might expect a very uniform mercury intrusion pressure corresponding to these recurrent neckings in the pore structure. Since the gold flashing could be 100 Å on top, less on the sides were measured, and both the SEM and the mercury penetration were subject to calibration, we felt this to be a gratifying agreement. I also marked and measured 120 pore widths at random, including enlargements, and these gave a mean pore diameter of 2440 Å, 24 percent greater. The slope also was greater, with standard deviation 850 Å up to 75 percent of the readings, and above that the plot bent sharply upward to 6000 Å diameter at 96 percent, due to multiple intersections. So with this picture I consider it likely that Casassa's and Alfrey's concept of the separation mechanism is in good agreement with my data.

In GPC theories the straight line calibration curve observed with the lower permeability gels is usually cited as the normal and proper thing. Although we all love to find nice straight lines, it is awkward that these have to become vertical at both ends. Let us