
Analytical Polymer Rheology

**Structure - Processing - Property
Relationships**

Charles L. Rohn



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Hanser Publishers, Munich Vienna New York

Hanser/Gardner Publications, Inc., Cincinnati

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Distributed in the USA and in Canada by
Hanser/Gardner Publications, Inc.
6600 Clough Pike, Cincinnati, Ohio 45244-4090, USA
Fax: (513) 527-8950
Phone: (513) 527-8977 or 1-800-950-8977

Distributed in all other countries by
Carl Hanser Verlag
Postfach 86 04 20, 81631 München, Germany
Fax: +49 (89) 98 12 64

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Library of Congress Cataloging-in-Publication Data
Rohn, Charles L.
Analytical polymer rheology: structure-processing-property
relationships / Charles L. Rohn
p. cm.
Includes index.
ISBN 1-56990-149-X
1. Polymers—Rheology. I. Title.
TP1092.R64 1995
668.9—dc20 95-5251

Die Deutsche Bibliothek – CIP-Einheitsaufnahme
Rohn, Charles L.:
Analytical polymer rheology : structure processing property
relationships / Charles L. Rohn. – Munich ; Vienna ; New
York : Hanser ; Cincinnati : Hanser-Gardner, 1995
ISBN 3-446-17034-0

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© Carl Hanser Verlag, Munich Vienna New York, 1995
Typeset in Ireland by Datapage International, Ltd., Dublin
Printed and bound in Germany by Kösel, Kempten

Rohn

**Analytical Polymer
Rheology**

*This book is dedicated to my wife,
Connie*

Preface

I was motivated to write this book because of my enthusiasm for using rheology for analytical purposes. Too many people think rheology is only for engineers and material scientists, and not for analytical chemists. Rheology, however, is a very sensitive probe of the molecular and morphological structure of matter.

The growth of rheology for analytical purposes has been impeded by the lack of understanding that mechanical perturbations at the surface of a body can give information on a molecular scale at the interior of materials. This is not the result of any oversight on the part of scientists. Rather, too few examples of these relationships exist in the literature. From my own studies, I have drawn examples to show how structure–processing–property relationships can be understood from rheology.

Another reason for rheology's limited use in chemical structural analysis is that theoretical rheology and applied rheology do not complement each other. To bring theory into wider practice, this book gives detailed step-by-step derivations of theories that are used in the text. This should give the reader a better appreciation of these theories and their applications.

The science of rheology, which is the study of the deformation and flow of materials, is built on the foundations of classical physics and mechanics. It dates back to Archimedes. The laws of levers and fluids in static equilibrium were known to the Greek scientists in the third century BC. The development of physics in the last three centuries, however, began with the discovery of the laws of mechanics by Galileo and Newton. The laws of mechanics were formulated by Newton and Hooke in the middle of the seventeenth century. Two hundred years later, James Clark Maxwell and Ludwig Boltzmann introduced theories to explain the nonideal behavior of solids and fluids. The fact that almost all materials are combinations of these two states of matter evolved into the theory of viscoelasticity and the Boltzmann Superposition Principle. The understanding that all matter exhibits solid–fluid duality brought about the new concept of relaxation and retardation phenomena. It is now well accepted that all materials possess relaxation and retardation times that are manifestations of the size, shape, spatial arrangements, and interactions among molecules.

Until now, the theory of linear viscoelasticity has given a mathematical description, based on mechanical models of springs and dashpots, to describe the spectrum of relaxation and retardation times exhibited by materials. Emphasis has definitely been placed on the purely mathematical side and not on any molecular

interpretation of spectra. This was acceptable before the molecular nature of the structure of matter was well established.

The determination of the molecular mass of gas molecules from transport processes was pioneered by Maxwell and Boltzmann through the development of the Kinetic Theory of Gases and the Distribution Law. Einstein and Staudinger were able to show the relationship of viscosity to hydrodynamic volume of suspensions and polymer solutes. The long-range elasticity and thermoelastic effects of rubber are explained by entropy changes that occur because of covalent bond angle distortions. Before this Theory of Rubber Elasticity, the Theory of Elasticity was the only explanation for the elastic nature of Hookean solids. The property of plasticity and fracture can be partially understood from the Hole Theory and Free Volume Theory. The Griffith Crack Theory has been successful in explaining the departure of brittle materials from their theoretical fracture strength.

As an industrial researcher, I understand the importance of the basic principles of industrial processes and the performance of products as viewed at the molecular level. As a teacher of plastics technology and manufacturing processes, I have used theories where possible to give students a greater understanding of the processing behavior of plastics and coatings and an appreciation of why one plastic is more suited than another for a given application from a physicochemical point of view. Rheology and chemistry have been focal in both my research and teaching.

Fortunately, I have been associated with scientists who have helped me to understand many of the structure–processing–property relationships of plastics and coatings. Professor H. Morawetz taught me the theory of the thermodynamic properties of polymer solutions. My laboratory partner, Dr. R. Stratton, exposed me to dynamic mechanical data of polymer blends. Professor A. Tobolsky helped me to understand the fundamental principles of rheology, relaxation, retardation, and dynamic mechanical spectra. I am indebted to Dr. J. Starita for employing me at Rheometrics and for the opportunity to work with state of the art rheometers. I also thank the New Jersey Institute of Technology for the experiences and rewards that come from teaching, and Dr. E. Immergut for encouraging me to write this book, which has been an intellectually stimulating experience.

Furthermore, I am indebted to my family for their generous assistance. David Rohn who installed and patiently maintained the computer that was used to produce this manuscript. Gail Boate who typed the initial draft of this manuscript. Unintimidated by mathematics, rheology, or chemistry, Barbara Sullivan willingly and carefully proofread every chapter for grammatical errors. Finally, I acknowledge with sincere gratitude Dr. T. A. Huang, who reviewed the manuscript for technical accuracy and offered many suggestions that were incorporated into the final version.

Above all, I thank God for everything I needed to finish this work.

Charles L. Rohn

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1

History of Rheology and Macromolecular Science

The curiosity of humans and the necessity to make things happen are the two main motivations for acquiring knowledge and advancing technology. They enable us to understand why an event is happening and give us the ingenuity to invent something new. To quote Democritus (c. 420 B.C.) The Intellect: "Apparently there is color, apparently, sweetness, apparently bitterness, actually there are only atoms and the void." The Senses: "Poor Intellect, do you hope to defeat us, while from us you borrow your very evidence. Your victory is in fact your defeat."

The word atom in Greek means "indivisible." The atoms are believed to be the ultimate and eternal particles of which all material things are made. Our knowledge of Greek atomism comes mainly from the poem by the Roman, Lucretius: "De Rerum Natura" (Concerning the Nature of Things), written 100 B.C. "The same letters, variously selected and combined signify, heaven, earth, sea, rivers, sun, most having some letters in common. But the different subjects are distinguished by the arrangement of letters to form the words. So likewise in the things themselves when the intervals, passages, connections, weights, impulses, collections, movement, order, and position of the atoms interchange so also must the things formed from them change." Another quotation from Lucretius gives reference to rheology: "We see how quickly through the colander the wines will flow; on the other hand, the sluggish olive-oil delays; no doubt, because 'tis wrought of elements more large, or else more crook'd and intertangled."

The atomic theory was not universally accepted until the Renaissance Period. Gassendi (1592–1655) introduced many of the concepts of present atomic theory. He believed that atoms are rigid, moving at random in a void and colliding with one another. Hooke extended this hypothesis and proposed in 1678 that the elasticity of a gas was the result of atoms colliding with the retaining walls. In 1738 Daniel Bernoulli correctly derived Boyle's Law by considering the collisions of atoms with the container wall. From this great work came the understanding that the total translational kinetic energy E of gaseous molecules is equivalent to Boyle's Law ($PV = C$ at constant temperature).

The scientific basis of rheology is classical mechanics. Our understanding of mechanics began with Galileo Galilei (1564–1642) and Sir Isaac Newton (1642–1727). Galileo published works developing the theories of Archimedes in mechanics. He attempted to discover the laws of falling bodies by a combination

of experiments and mathematical reasoning. Eventually this led to the correct formulation of the acceleration due to gravity. About 1609, or possibly later, Galileo discovered that the velocity of a falling body increases in proportion to time. He also observed that in air heavy bodies fall faster than lighter ones, although he could not prove or disprove that the same would be true in a vacuum.

Other great work during the seventeenth century was done by Hooke and Boyle. Within a few years, three laws of science evolved: Hooke's law (1678), Newton's law (1685), and Boyle's law (1660). Hooke introduced the rheological behavior for an ideal solid. Newton introduced the behavior of an ideal liquid. Boyle established that pressure is inversely proportional to the volume of gases. The modern concept of air as a fluid goes back to the early seventeenth century, when Torricelli, Pascal, and Boyle first established the physical nature of the air. This was the turning point in changing scientific attitude toward the mechanocorpuscular view of nature that is associated with the thinking of Galileo, Boyle, Newton, and others. Henceforth, scientists started to look for explanations based on matter and motion.

Boyle's research was carried out to illustrate not just the quantitative fact that air has elasticity, but also that air can exert mechanical pressure strong enough to support considerable weight. His achievements introduced a new dimension into physics—pressure. In his *Philosophiae Naturalis Principia Mathematica*, Newton briefly discusses the consequences of various hypotheses about the forces between atoms and the relation between pressure and volume. It appears that Newton was trying to put Boyle's law into mathematical terms, and that he thought repulsive forces were due to the action of atomic springs in contact with each other. Without any experimental evidence, the question remained unanswered for over a century.

The advancement of the molecular theory of gases came to a virtual standstill during the eighteenth century. Brilliant mathematicians refined and added support to Newton's principles of mechanics and applied them to the analysis of the motion of celestial bodies and of continuous solids and fluids. The atoms in a gas were still thought of as being suspended in the ether, although they were believed to vibrate and rotate.

About the same time the caloric theory was being brought to its final stages by Laplace, Poisson, Carnot, and Clapeyron. John Herapath attempted to explain the molecular properties of gases and such other seemingly unrelated phenomena such as changes of state. His theory was rejected by Humphry Davy as too speculative. By the middle of the nineteenth century, James Clark Maxwell, Clausius, O.E. Meyer, and P.G. Tait developed the theory of diffusion, viscosity, and heat conduction on the basis of the modern kinetic theory of gases.

The foundation of the modern theory of transport was laid by Maxwell in his great memoir of 1866. It is essentially this work that Boltzmann used to make his discoveries. Maxwell wrote down general equations for the rate of change of any quantity at any point in space and time resulting from molecular motions and collisions. These microscopic equations were then compared with the corresponding macroscopic equations, like the Navier–Stokes equations of hydrodynamics and

the coefficients of viscosity. This was the beginning of our understanding of classical physics and rheology.

Boltzmann's transport equation, derived in 1872, is a special case of Maxwell's general equation, in which the quantity of interest is the number of molecules having a certain velocity. This is the velocity distribution of gas molecules. Boltzmann also concluded from this work that entropy and probability are related.

During this period, van der Waals published his work on the continuity of liquid and gaseous states. His theory is not based on the kinetic theory of gases, because it does not take molecular motion of gases into consideration; only the volumes and interaction are considered.

The kinetic theory of gases could not satisfactorily explain many experimental observations, such as the specific heats of polyatomic gases. Explanations like "energy surfaces" and the "ergodic hypotheses" were given to account for the deficiencies of the kinetic theory.

The struggle to understand whether atoms exist or not was intense. For one, Boltzmann became deeply troubled over what appeared to be the inadequacies of the kinetic theory to explain the properties of gases in atomic and molecular terms. This led to his suicide in 1906. Ironically, if Boltzmann had lived for a few more years he would have seen a complete turnaround in the acceptance of atomic theory. Even Ostwald, who incorrectly believed in colloidal states, changed his thinking. By 1909, atomism came alive.

Boltzmann is known primarily for his pioneering work in statistical mechanics and our understanding of entropy. His contribution to rheology is also of great significance. He developed the Boltzmann Superposition Principle, which is one of the most important concepts for relating the mechanics of materials to their molecular structure. Since it is not satisfactory to have material properties that depend on the type of test or test conditions, research efforts were directed toward unifying all the data from different experiments. This was found to be feasible with the introduction of the Boltzmann Superposition Principle. Boltzmann in 1876 suggested that small changes in stress are equal to small changes in modulus multiplied by the strain. This means that the modulus is independent of the amount the material deforms. Embodied in this principle is the linearity of viscoelasticity. Within the limits of the linear viscoelasticity is a coherent phenomenological theory.

Equally as controversial was the thinking that polymers do not exist as a single molecule. The covalent bond was not understood, and the idea that the molecular weight of matter changed with its state led to great confusion. For example, rubber was believed to be made up of "association colloids." Faraday in 1826 proposed the empirical formula C_5H_8 with one double bond for rubber. Based on the knowledge that inorganic substances can behave as colloids, it was believed that this colloid state applied to organic materials that appeared to form similar aggregates. It was postulated that colloids had peculiar binding forces—small rings held together by "partial valance" bonds. This was called the "first micellar theory." It could not be comprehended that large molecules held together by covalent bonds could exist.

Staudinger opposed this view and worked tenaciously to prove that polymers are macromolecules. In 1922, Staudinger and Fritsch hydrogenated rubber.

Because hydrogenated rubber no longer contains double bonds, it should not form colloids. This is one of the criteria of the micellar theory. Staudinger is given credit for pointing out many inconsistencies in the associated colloid theory, and promoting the idea that polymers are chain macromolecules made of monomers connected by covalent bonds. This prompted other researchers, like Meyer, Mark, Fischer, and Carothers, to prove that the associated colloid theory was false. Also, Staudinger deserves credit for emphasizing that the molecular weight of a linear polymer may be determined by measuring its dilute solution viscosity. During that time, E.O. Kraemer and G.R. Sears reviewed many of the explanations about the molecular weight dependence of the solution properties of polymers. They took the analysis one step further by calculating the intrinsic viscosity of solutions of nitrocellulose. They concluded, based on Einstein's equation of dilute suspensions, that the solutes are swollen with solvent and that the hydrodynamic volume is 100 times larger than what it should be based on molecular weight consideration. This view is very similar to Zimm's hydrodynamic theory of solvated polymers.

Eugene Bingham, founder of the Society of Rheology, published a number of papers pertaining to viscosity measurements and the interpretation of atomic structure and molecular association of low molecular weight fluids. He favored the free volume theory proposed by A. Batschinski, in which fluidity is a linear function of specific volume. From this time on, studies by Mark, Kuhn, Debye, Bueche, Flory, Rouse, Zimm, and others brought the theory of the solution properties of polymers to its final stage of development. Special credit goes to Flory for his contribution to our understanding of the molecular rheology of dilute solutions of macromolecules.

As long ago as 1913, Batschinski made the connection between the viscosity of liquids and their specific volume. He showed a proportionality between fluidity (reciprocal viscosity) and free volume. Subsequent work by Kirkwood, Frenkel, Eyring, Doolittle, and Macleod showed that free space within liquid bodies allows the molecules to move about relatively freely compared to molecules in their solid state.

Free space in solids has a different physical meaning than in liquids. In solids, interstices and defects in crystals have a definite size and shape. In liquids, density fluctuations cause increases and decreases in the intermolecular distances, thereby distorting the homogeneity of the body in small volumes.

Prior to the work of Doolittle, Eyring showed that the Theory of Absolute Reaction Rates can be applied to viscosity and diffusion in liquids. He refers to "holes" or free volume in liquids. This theory has also been applied to diffusion in crystals as well as amorphous materials.

By the end of the nineteenth century, the science of fluid mechanics was developing in two different directions. One was the science of theoretical hydrodynamics, which evolved from Euler's equations of motion for a frictionless, nonviscous fluid and which achieved a high degree of completeness. Because the results did not agree with the experimental results, such as predicting pressure losses in pipes, hydraulics developed. This science is based largely on experimental facts. By the beginning of the twentieth century, L. Prandtl showed how to unify these two diverging fields. He achieved a high degree of agreement between theory and