Chapter 2
Flory and Friends

High Polymers: Volume 1 "Collected Papers of Wallace Hume Carothers on High Polymeric Substances"

Although Wallace Carothers (1896-1937) was not alive to personally interact with the ongoing polymer science community, he left a legacy of publication that was quickly collected and edited by Herman Mark (1895-1992) and G. Stafford Whitby (1887-1972). It was issued in 1940 as Volume 1 in the Interscience series: "High Polymers" [1]. A short biography condensed from the official National Academy of Sciences version by Roger Adams (1889-1971) is included. The education of Wallace Carothers was greatly assisted by his time at the University of Illinois. In addition to research with Adams, Carothers was retained as an instructor until 1926. He was acclaimed as "one of the most brilliant students who had ever been awarded the doctor's degree at Illinois." He was then appointed to the Chemistry Department at Harvard University. James B. Conant (1893-1978), Professor of Organic Chemistry and later President of Harvard, rated Carothers very highly for his originality. While Carothers would go on to become famous for polymer chemistry, he was at the top of his field, both experimentally and theoretically, in synthetic and physical organic chemistry. It was his thorough grounding in the fundamentals of organic chemistry that enabled him to make rapid progress in his understanding of polymerization.

Developments at DuPont opened new avenues in research for Carothers. He was hired in 1928 to direct a new laboratory of organic chemistry at the Experimental Station in Wilmington, Delaware. Dr. Elmer K. Bolton (1886-1968), Chemical Director of DuPont, was "impressed by the breadth and depth of his knowledge." Carothers wasted no time in pursuing the field of experimental synthetic polymer chemistry. His first paper on polymerization appeared in the *Journal of the American Chemical Society (JACS)* in 1929 [2]. It was already a masterpiece of clear thinking and encyclopedic presentation. Whereas

G. Patterson, *Polymer Science from 1935–1953*, SpringerBriefs in History of Chemistry,
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Staudinger was always rather confused in exposition, Carothers was both precise and elegant. A flurry of experimental work was summarized in the monumental paper entitled "Polymerization" published in 1931 in *Chemical Reviews* [3]. The basic principles of condensation polymerization were established beyond dispute. The whole landscape of polymeric substances was considered in detail. Any coupling reaction that was known to chemistry could be used in the synthesis of a polymer.

Carothers also extensively studied polymers formed by radical reactions involving unsaturated monomers. He made special contributions to systems involving both double and triple bonds. One of his earliest discoveries (1931) yielded the important rubber, polychloroprene [4]. He systematically investigated the influence of substituents on the reactivity of butadienes. Carothers carried out polymerizations of vinylacetylene and divinylacetyalene.

Chloroprene polymerizes thermally to yield a true rubbery solid with a characteristic liquid-like structure. Stretching produces crystallinity and the expected X-ray pattern for an oriented fiber. A detailed mechanistic analysis yielded the multiple structures that appear during the reaction. Another synthetic pathway leads to polychloroprene latex. Characterization of these particles with the ultracentrifuge yielded a highly peaked distribution with a mean radius near 0.06 micron. Because of the very small particle size compared with natural rubber latex, this material can be used for many applications requiring minute particles. The detailed analysis and keen structural insight set a standard that is rarely met, even today.

The final paper in "The Collected Papers of Wallace Carothers on Polymerization" is the classic plenary lecture at the Faraday Discussion of 1935 reviewed in "A Prehistory of Polymer Science" [5]. Just as Humphry Davy's greatest gift to Chemistry was Michael Faraday, Wallace Carothers revealed in this paper that there was a new scientist working on fundamental properties of polymers: Paul John Flory (1910-1985).

Paul John Flory (1910-1985)

Flory was also from the Midwest and attended Ohio State University (Ph.D. 1934). His class notebooks reveal a lively and inquiring mind. He wrote his thesis on the photochemical decomposition of nitric oxide. A thorough grounding in chemical kinetics was the perfect preparation for his work with Carothers at DuPont. It was known that condensation polymerization produced a broad distribution of molecular weights. Flory was able to calculate from first principles the distribution of chain lengths for a system of reacting molecules as a function of extent of reaction, p. This paper appeared in *JACS* in 1936 [6]. The "most probable distribution law" for the distribution of x-mers is one of the foundations of polymer science: $\Pi_x = xp^{x-1}(1-p)^2$, where x is the number of monomer units in the polymer.

Once the concept of a distribution of chain lengths is accepted, the need to take into account the effect of this distribution on measured properties becomes apparent. Flory derived the number average distribution, the weight-average distribution and the z-average distribution. The number average distribution of chain lengths is the usual linear distribution where each chain length is weighted by the number fraction of chains in the total sample. Some physical properties depend on the weight fraction associated with each chain length. The z-fraction is the next higher weighting that depends on number fraction times the square of the chain length. From these distributions he calculated the number average molecular weight, the weight average molecular weight and the z-average molecular weight. Experimental properties such as the intrinsic viscosity depend on higher molecular weight averages. Staudinger had made limited progress in understanding the interpretation of the viscosity; it was time for leaders that understood physical chemistry.

Werner Kuhn (1899-1963)

Werner Kuhn (1899-1963) brought the power of theoretical chemical physics to the study of polymers. Kuhn was educated at the Eidgenossiche Technische Hochschule (ETH) in Zurich, Switzerland and received his doctorate in physical chemistry at the University of Zurich in 1923. He worked in many of the best laboratories in Europe, but with the approach of the War, he retreated to the University of Basel's Institute of Physical Chemistry in 1939. Kuhn was thoroughly familiar with the theory of molecules that developed in Europe in the 1930s. On this basis he proposed in 1936 that chain molecules in solution can be modeled as a random coil [7]. The chain molecule is represented in terms of vectors associated with each main chain bond. This model assumes that the direction of the main chain bonds eventually becomes uncorrelated when the distance along the chain becomes large. Kuhn worked out the mathematical consequences of this model in a form that is still used today. He was then able to use the random coil model to explain the source of the retractive force in rubber elasticity. The random coil model also allowed the problem of polymer solution viscosity to be attacked. Staudinger was just wrong on this subject. It took a real theorist to develop a real theory.

Polymers formed from unsaturated monomers also lead to distributions of molecular weight. But, the mechanism of the radical reaction was not yet well understood. Again, Flory's thorough background in chemical kinetics provided the insight to realize that individual growing chains could terminate by chain transfer to monomer or other chains. The classic paper on "The Mechanism of Vinyl Polymerization" appeared in *JACS* in 1937 [8]. The mechanism of vinyl polymerization had been considered by Staudinger [9], and by Dostal and Mark [10], but their theories did not agree with the experimental facts. The rate of the reaction increases with time as the concentration of radical centers increases. The average molecular weight of the formed polymers is relatively constant over much of the reaction. While the termination reactions due to radical coupling or disproportionation were well known for small molecules, these processes removed radicals from the reaction and would not lead to an increase in the rate. It was the proposal that individual chains could terminate by chain transfer that solved the problem. The radical center was merely transferred and remained active for further polymerization on another center. Paul Flory was not a one hit wonder!

With the death of Carothers, the character of the research laboratory at DuPont changed [11]. There was now no one devoted to fundamental research for its own sake, even in the pursuit of industrially relevant knowledge. Flory chose to leave DuPont and joined the Basic Sciences Research Laboratory of the University of Cincinnati in 1938. He continued his studies of the mechanisms and chain length distributions of polymers.

Another class of polymers grows by sequential addition of monomers without possibility of termination. The classic paper by Flory on the "Molecular Size Distribution in Ethylene Oxide Polymers" appeared in *JACS* in 1940 [12]. These polymers are observed to have a very narrow distribution of chain lengths. Flory was able to use statistical arguments in connection with the correct mechanism for these reactions to derive the Poisson distribution for the chain length:

$$\wp(x) = e^{-v}\, v^{x-1} \,/\, (x-1)!$$

where ν is the number average chain length less 1. The paradigm of molecular weight distributions was now firmly established and remains an essential part of every discussion of polymeric systems.

Another polymeric phenomenon that was attacked by Flory while at Cincinnati was the structure and formation of gels [13]. It had been known for many years that when a trifunctional or higher monomer was polymerized with a difunctional monomer, the system eventually became a three dimensional soft solid. At a well-defined point during the reaction the viscosity of the material diverged to infinity and the shear modulus started to rise above zero. Flory used statistical arguments and a keen understanding of the mechanism of the gelation reaction to derive relationships between the extent of reaction, the actual stoichiometry of the polymer network and the critical probability of infinite network formation. For a branching unit of functionality f, the critical value of the probability is: $\alpha_C = 1/(f-1)$. At the gel point, the system still contains mostly unreacted monomer and a distribution of smaller polymers. The "sol" fraction then decreases as the reaction proceeds. A detailed calculation of the chain length

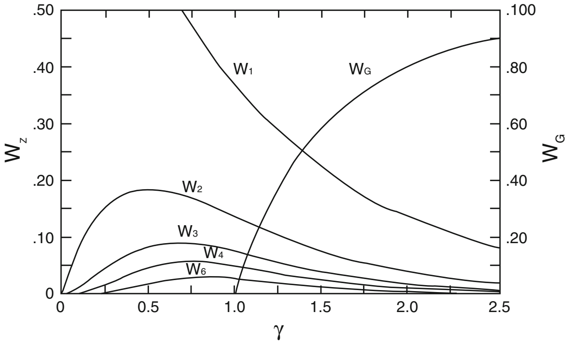


FIG. 3. Weight fractions (W_z, left ordinate scale) of species composed of one, two, three, four, and six chains *versus* cross-linking index γ . Weight fraction of ge, W_g (right ordinate scale).

Fig. 2.1 Gelation diagram from Flory [14] (J. Phys. Chem. by permission)

distribution in the sol followed in a second paper (See Fig. 2.1). And the calculations were extended to tetrafunctional junctions in a third contribution. This work was presented and summarized in a classic article in the *Journal of Physical Chemistry* in 1942 [14]. By this time Flory had joined the Esso Laboratories of the Standard Oil Development Company in Elizabeth, New Jersey. He was free to pursue a wide range of problems in this position. And he did!

Esso Laboratories

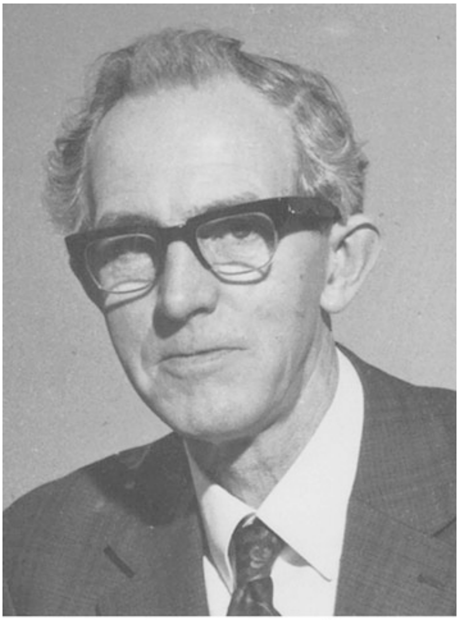
One of the other extensive areas that Flory pursued at Esso was the thermodynamics of polymer solutions. The general theory of two component liquid mixtures was still in its infancy in 1940. A series of papers by Flory published in the *Journal of Chemical Physics* changed all that. The first major contribution (1941) was the derivation of an expression for the entropy of mixing that included the **volume fraction** rather than the mole fraction of the solvent [15]. Standard physical chemistry texts still fail to acknowledge this feature, but all industrial laboratories use the correct Flory expression to obtain osmotic pressures that agree with experiment! A much more extensive paper that included the full discussion of the so-called Flory-Huggins theory appeared in 1942 [16]. It included a calculation of the two component phase diagram for partially miscible liquids that was at least qualitatively correct. Flory discusses in detail the limitations of the theory: random mixing is assumed, the volume change on mixing is ignored.

Geoffrey Gee (1910-1996)

Reference is made in this paper to another emerging leader, Geoffrey Gee (1910-1996, FRS). Gee was educated at the University of Manchester (M.Sc. 1933) and at Cambridge University (Ph.D. 1936) with Sir Eric Rideal (1890-1974, FRS). His work was much appreciated and he stayed on for a postdoctoral fellowship until 1938. He became an expert in the chemical kinetics of thin films. These were the glory years in the Rideal Laboratory at Cambridge. Sir Harry Melville (1908-2000, FRS, KCB) was also with Rideal at this point. Gee then joined the British Rubber Producers Research Association (BRPRA) as a Senior Physical Chemist. He carried out a program of fundamental research on the structure and properties of natural rubber. Another leading figure in the study of the physical properties of rubber at the BRPRA was L.R.G. Treloar (1906-1985). His monograph "The Physics of Rubber Elasticity" is still considered an essential volume [17]. Consideration of the osmotic pressure of rubber solutions and the swelling of crosslinked rubber led Gee to make some of the best thermodynamic measurements then published. They impressed Flory and the two men went on to become great friends. Gee could approach Flory as an equal and they were scientifically good for one another. It took more than simplified theory to create a sound foundation for polymer science. Flory always put more faith in the experiments than the theory, but he did try to understand polymer solutions and swollen rubber in the best quantitative way he could. He never stopped creating better theories of polymer solutions and gels. One of the foundational papers in polymer science is Gee's review in the initial volume of the *Quarterly Reviews of the Chemical Society* (1947) on "Some thermodynamic properties of high polymers and their molecular interpretation" [18]. Gee's Royal Society biographical memoir was expertly written by one of his most famous colleagues, Sir Geoffrey Allen (1928-, FRS) (Fig. 2.2).

One of the most pressing problems in polymer science in the early 1940s was the quantitative theory of rubber elasticity. Substantial conceptual progress had been made by Kuhn and by Eugene Guth (1905-1990) and Herman Mark (1895-1992), but a readily applicable expression was needed to guide further work. Flory collaborated with John Rehner Jr. (1908-1997) on a classic series of papers on polymer networks and gels. The random coil model was now accepted as a good part of the paradigm. Flory considered in detail the role of the network in the theory. The distribution of crosslink sites is deformed by the macroscopic deformation; Flory assumed an affine deformation. The distribution of end-to-end vectors for the elastically effective chains is modified by the network and the detailed equations are given. The new insights continued the development of the theory of rubber elasticity [19]. It is still not "finished."

With both a workable theory for network deformation, and a semi-quantitative theory of polymer solutions, Flory and Rehner tackled the problem of swollen rubber [20]. Their combined theory is so good, that it is still used in industry, even though there are serious problems at the most fundamental level. They even correctly described the change in the elongational modulus due to swelling. It is clear that Esso Laboratories provided a scientifically productive work environment.



Geoffrey Gee

Fig. 2.2 Sir Geoffrey Gee (FRS) (University of Manchester, by permission)

Goodyear Tire and Rubber Company

The large body of work produced at Esso vaulted Flory into a position of intellectual leadership in the polymer community. In 1943 Goodyear Tire and Rubber Company offered Flory an administrative leadership position as Head of its fundamental polymer research group in Akron, Ohio. It was a mutually beneficial situation.

Early in 1944 a symposium on the “Theory of Long-range Elasticity” was held at the Cleveland Meeting of the American Chemical Society. Flory’s plenary lecture, “Network Structure and the Elastic Properties of Vulcanized Rubber”, was published in *Chemical Reviews* [21]. It summarized all the work done through 1944 and presented new comparisons between theory and experiment. The classic case of the elongational modulus and its dependence on swelling is shown in Figure 8 from that paper (Fig. 2.3). It is based on the Flory-Rehner equation:

$$\tau \cong RT\left(\alpha - 1/\alpha^2\right)((1/2) - \chi)/\varphi_2^{5/3}\,\bar{V}_1$$

where α is the linear deformation, φ_2 is the volume fraction of the polymer, χ is the Flory interaction parameter, and V_1 is the molar volume of the swelling solvent. The slope of the line is well within the experimental error of -5/3! The calculation for the equilibrium swelling ratio was also successful. Goodyear was thrilled!

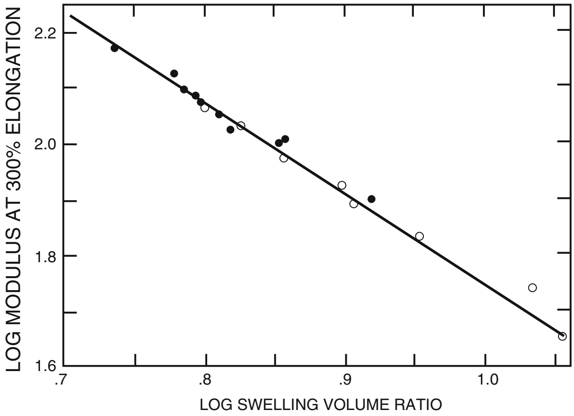


FIG. 8. Relationship between "modulus" and swelling volume ratio ($1/v_2$) for various pure gum Butyl vulcanizates. ○ = low unsaturation series; ● = high unsaturation series.

Fig. 2.3 Elongational modulus as a function of swelling [21] (Chemical Reviews, by permission)

Flory was also tapped to produce a critical review article on "Condensation Polymerization." It became the basis for his Baker Lectures at Cornell and for several chapters in his book, "Principles of Polymer Chemistry."

Ever eager to make actual progress in understanding, Flory considered the serious discrepancy between the Flory-Huggins theory and actual data when the concentration of polymer was below a critical concentration, now known as c*. Under these conditions, the polymer concentration inside the **pervaded volume** of individual chains was c*, while it was 0 elsewhere. Thus, the initial slope of a plot of osmotic pressure against concentration was far lower than predicted by the "mean-field" theory. Even the curvature was incorrectly predicted. It was time for a better theoretical approach. The initial paper in this series was written at Goodyear, and clearly makes the case for the phenomenological understanding; it even achieves a modest agreement with experiment by using a perturbation theory of interaction between polymer coils [22].

Another phenomenon that was of interest to Goodyear was the strain-induced crystallization of natural rubber. It was another chance to apply both the theoretical expertise developed by Flory over the last decade and the deep intuition gained from experimental work in the industrial environment. (Flory once demonstrated for me how to determine the average molecular weight of bulk polyisobutylene from the tackiness of the liquid sensed with his own hand.) Melting points of liquids are functions of pressure, and the quantity (dT_m/dP) depends on the sign of the volume change on melting through the Clapeyron equation. The melting temperature can also be manipulated by changing the entropy of the liquid phase through orientation. Since the chemical potential of the liquid phase is increased relative to the crystalline phase, the melting temperature is raised. Flory derived a

Fig. 2.4 Degree of crystallization as a function of elongation at different temperatures [23] (J. Chem. Phys., by permission)

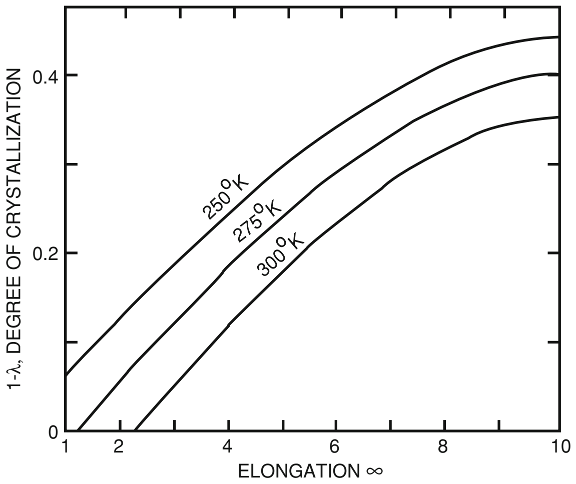


FIG. 1. Degree of crystallization $(1-\lambda)$ at equilibrium
elongation at the three temperatures indicated. Curves
culated from Eq. (18) taking $n=50$, $h_f=600R$ and
$=250°$K.

statistical mechanical theory for the entropy of the liquid phase under uniaxial stretching. He then constructed a phase diagram for the equilibrium degree of crystallinity as a function of elongation. The result is shown in Fig. 2.4. At the lowest temperature, the crosslinked rubber crystallizes to some degree in the relaxed state. Unlike a macroscopic phase of a pure liquid, the crosslinked rubber does not completely crystallize in the relaxed state. The crosslinks are excluded from the crystal lattice. As the sample is oriented by elongation, it can crystallize further since the chemical potential of the liquid is increased. At the highest temperature, the sample will only crystallize when sufficient elongation is produced. Clear theory; clear presentation; semi-quantitative agreement [23].

Thomas G Fox (1921-1977)

Work on the problem of crystallization also introduced Flory to one of his best colleagues and friends, Thomas G Fox (1921-1977). Fox received his Ph.D. in physical chemistry from Columbia University in 1943. After military service he joined the Goodyear Tire and Rubber Company in 1946. His first joint paper with Flory appeared in 1948. It was the first of many joint papers on the temperature and molecular weight dependence of viscosity.

Cornell University

The Cornell University Chemistry Department had a marvelous tradition that improved the intellectual environment of the place and served as a recruiting tool for the best people. In 1948, Peter Debye (1884-1966) invited Paul Flory to be the George Fisher Baker Non-resident Lecturer. In addition to giving a series of lectures, he brought along Tom Fox to continue their highly productive collaboration. Debye was one of the most famous scientists in the world and received the Nobel Prize in Chemistry in 1936. From 1934-1939 he was the Director of the Kaiser Wilhelm Institute in Berlin. But, in 1939 he accepted an offer to be the Baker Lecturer at Cornell, and never left. He became the Chair of the Chemistry Department at Cornell and dramatically improved the quality of research carried out there. With regard to polymer science, Debye developed the theory and technique of light scattering as a method for measuring the molecular weight and molecular size of polymers in solution. Flory also followed the tradition of remaining at Cornell as a Professor, his first real academic appointment.

William Krigbaum (1922-1991)

The academic position at Cornell allowed Flory to attract outstanding collaborators and Flory hired William Krigbaum (1922-1991) as a Postdoctoral Fellow. Krigbaum went on to have a brilliant career at Duke University. Flory's interest in the properties of dilute polymer solutions continued at Cornell and a major paper appeared in 1949 on the configuration of real polymer chains [24]. His work on this problem was greatly aided by Debye, who had used the Gaussian chain model of Kuhn to calculate the single chain scattering function of light scattering, S(q). This problem, known as the "excluded volume" problem, can be approached from several perspectives. The first concept is to consider the change in the dimensions of the chain due to the obvious fact that two segments cannot occupy the same space. Flory distinguished two cases: 1) local interactions that do not depend on molecular weight, and 2) long range interactions of segments separated by many units along the chain contour. If the true molecular chain is idealized as a sequence of Z statistical subunits comprised of many mers, two subunits can share the same center-of-mass location. The local interactions will affect the chain dimensions, but it will be reflected in a change in the "statistical segment length" in the Kuhn model. The long range interactions will depend on the molecular weight, since the average density of statistical segments is a function of the number of segments in the chain as a whole. For N statistical segments distributed in space around the center–of-mass in a Gaussian function, the average density of segments for an "unperturbed chain" will scale as $N/R_G^3 \sim N^{-1/2}$. When it is realized that the actual average radius of gyration is increased since chains with small radii of gyration will have a higher interaction probability, the expansion factor, α, can be expressed as:

$$\alpha^5 - \alpha^3 = C Z^{1/2}$$

where C is a constant and Z is the number of subunits in the chain. In the limit of large expansion, the radius of gyration increases as $Z^{0.6}$.

Another concept is to treat each individual chain as a thermodynamic system subject to elastic energies of expansion and thermodynamic free energies of dilution by solvent. With both the theory of elasticity and the concept of the interaction of two subunits as a mixing phenomenon, the highly repulsive limit derived by the first method was extended to include solvents where the interaction energy for chain subunits was more favorable than the interaction with the solvent.

$$\alpha^5 - \alpha^3 = C(1 - 2\chi)Z^{1/2}$$

where the interaction parameter, χ, is from the solution theory. When the polymer molecular segments and the solvent are very similar, the interaction parameter is small and the previous result is obtained, but when the solvent becomes poor, the interaction parameter can become large enough that the chain has its "unperturbed" average radius of gyration. It is not that the chain subunits do not interact; it is equivalent to the Boyle point in a real gas where the repulsive and attractive forces balance. The "excluded volume" between statistical subunits vanishes at a particular temperature for the polymer-solvent pair; this is now called the Flory temperature or Θ.

The time for a viable interpretation of intrinsic viscosities of polymer chains in solution was at hand. Werner Kuhn published many of the key insights for this problem. Einstein calculated from classical hydrodynamics that the intrinsic viscosity

$$[\eta] = \lim_{c \to 0} ((\eta - \eta_0)/\eta_0 c) = 2.5\,(4\pi/3)\,R_e^3/M$$

depends on the hydrodynamic volume of a sphere of radius R_e. Kuhn proposed that for a high molecular weight chain, the solvent inside the coil would be entrained by the local frictional interactions, and hence the equivalent sphere would be proportional to the cube of the radius of gyration for the chain. This is now called the non-free draining chain. Flory then used his new quantitative relationship for the dependence of the radius on solvent quality and chain length to predict that the intrinsic viscosity would scale as $M^{1/2}$ in a Flory solvent and up to $M^{0.8}$ in a "good" solvent [25]. This agrees with the experimentally determined intrinsic viscosities for many polymer-solvent pairs! While a few subtleties remained, the basic conceptual picture has remained a pillar of polymer science.

A formally exact theory for the osmotic pressure of a dilute polymer solution can be constructed along the lines developed for dilute gases [26]. The key quantity needed for this approach is the potential of mean force between two full polymer coils in solution, $U(R_{12})$. The osmotic pressure can be expressed in dilute solution in the form:

$$\pi/c = (RT/M_n)(1 + A_2 M_n c + \cdots)$$

where

$$A_2 = \left(\frac{N_A}{2M^2}\right)\int_0^\infty \left(1 - \exp\left(-\frac{U(R_{12})}{k_b T}\right)\right)4\pi R_{12}^2 dR_{12}$$

The potential of mean force for the chains as a whole is proportional to the excluded volume for a pair of subunits, V_e. This potential is given by:

$$U(R_{12}) = 2k_b T Z^2 V_e \left(\frac{3}{4\pi\langle R_G^2\rangle}\right)^{3/2} \exp\left(-\frac{3R_{12}^2}{4\langle R_G^2\rangle}\right)$$

While the Flory-Krigbaum potential is not exact, it is in closed form and enabled them to evaluate the integral and obtain:

$$A_2 = \left(\frac{N_A Z^2 V_e}{M^2}\right)$$

This result does not quite agree with experimental data as a function of molecular weight, since A_2 decreases weakly at higher values of Z. The Flory-Krigbaum potential is not quite correct, and a mean field approach is not quite right. But, the major improvement in the understanding of the second osmotic virial coefficient obtained by them remains a monumental achievement.

T. G Fox continued his studies of the temperature and molecular weight dependence of the shear viscosity of polyisobutylene. A monumental paper appeared in 1951 in the *Journal of Physical and Colloid Chemistry* [27]. Fox is now listed as present at Cornell. A thorough examination over a very wide range in molecular weight revealed that at high enough molecular weight the isothermal shear viscosity at 217 C could be described by:

$$\log\eta = 3.40\log M - 13.56$$

A similar expression was found for polystyrene and the graph is shown in Fig. 2.5. It would be many years before the 3.4 power law observed at high molecular weight was explained, but the phenomenological standard had been established.

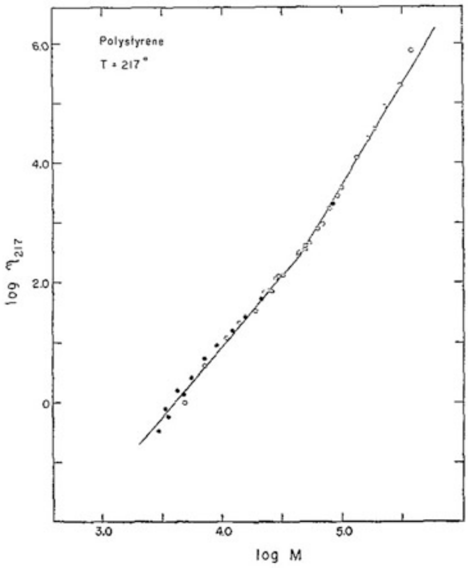


Fig. 10. Log η_{217} vs. log M for polystyrene fractions (6, 8). The straight lines correspond to equations 12 and 13.

Fig. 2.5 Log-log plot of viscosity against molecular weight [27] (Journal of Physical and Colloid Chemistry, by permission)

Another phenomenon associated with T. G Fox was the glass transition. A classic paper with Flory appeared in the *Journal of Applied Physics* in 1950 on the behavior of fractions of polystyrene as a function of temperature near the glass transition [28]. At this point, Fox and Flory referred to the observed phenomenon as a "second-order transition," a designation they would live to regret. Specific volumes were measured as a function of temperature on each fraction and the temperature where the thermal expansion coefficient showed a break in slope was taken as the glass transition temperature, T_g. An empirical correlation was constructed for this data.

$$T_g(K) = 373 - 1.0 \times 10^5/M$$

Equations of this type are now known as Flory-Fox equations. The quality of the data collected by Fox was so high that, like Faraday of old, it is still considered the best.

Cornell was a scientifically exciting place in the 1940s. Debye was leading a good corps of researchers in many directions. Since the random coil model was now an accepted paradigm, Debye explored the quantitative aspects of polymer chain configurations. He related the mean-square end-to-end distance and the mean-square radius of gyration, $\langle R_G^2 \rangle$. He even used this model to calculate exactly the single chain scattering function, now known as the Debye function:

$$S(q) = \left(2/u^2\right)[u - 1 + \exp(-u)]$$

where $u = q^2 \langle R_G^2 \rangle$. The scattering vector, $\vec{q}$, has a magnitude $q = (4\pi n/\lambda) \sin(\theta/2)$. The best values of the mean-square radius of gyration are obtained by measuring the entire function, not just the low angle limit.

One of the other Professors at Cornell during the 1940s was John Gamble Kirkwood (1907-1959). He developed an interest in the viscoelastic properties of fluids and applied his insights to polymer chains in solution. He applied the Oseen formulation of hydrodynamics rigorously to a chain composed of Z centers of frictional resistance. Kuhn's insight that the high molecular weight coil would entrain the pervaded solvent was given a quantitative basis. All the current work in single chain hydrodynamics is based on this pioneering work of Kirkwood [29].

Fox and Flory then applied the work of Kirkwood and Riseman to the problem of intrinsic viscosities in polymer solutions. They were able to use the single chain expansion theory of Flory and Krigbaum to derive a simple expression for the intrinsic viscosity in the high molecular weight limit:

$$[\eta] = \Phi \frac{\langle R^2 \rangle^{3/2}}{M}$$

where $\Phi = 3.62 \times 10^{21}$ is a universal constant, independent of polymer and temperature.

All the characteristics are then contained in the behavior of the mean-square end-to-end distance or the mean-square radius of gyration. In the good solvent limit, the intrinsic viscosity is predicted to scale as the 0.8 power of the molecular weight due to the strong expansion of the coil. For a globular coil, such as a protein, the intrinsic viscosity is independent of molecular weight. For a rodlike polymer, such as Staudinger proposed, the intrinsic viscosity is predicted to scale as the square of the molecular weight [30]. So much for the Staudinger viscosity law! The team of Kuhn, Debye, Bueche, Kirkwood, Riseman, Fox, Flory and Krigbaum established the actual paradigm for intrinsic viscosity. An immediate reward for Thomas G Fox was appointment as Director of Research at the Rohm & Haas Company in 1950 (Fig. 2.6).

Another of the major figures in polymer science to collaborate with Flory at Cornell was Arthur M. Bueche (1920-1981). He received his Ph.D. in Physical Chemistry with Debye on the conformational and frictional properties of polymers in solution. He became an expert on light scattering from polymer solutions.

DR. THOMAS G. FOX

Fig. 2.6 Thomas G Fox (Carnegie Mellon University, by permission)

A classic paper with Fox, Flory and Bueche on osmotic and light scattering data appeared in *JACS* in 1951 [31]. Bueche went on to become a star at the General Electric Company, a member of the National Academy of Sciences and was nominated as the Presidential Science Advisor.

Leo Mandelkern (1922-2006)

One of Flory's closest personal friends, Leo Mandelkern (1922-2006), joined him at Cornell in 1949 as a Research Associate after completing his Ph.D. at Cornell with Franklin Long. Mandelkern benefitted from interactions with Debye, Kirkwood, Scheraga and Flory. He became one of polymer science's leading experts on crystalline polymers, an area he pioneered with Flory. He went on to spend a decade at the National Bureau of Standards from 1952-1962. One area of special interest at Cornell was the use of frictional methods like diffusion, sedimentation and intrinsic viscosity to characterize polymer chains in solution [32] (Fig. 2.7).

With the torrent of papers flooding from the Flory laboratory, the time had come to prepare his Baker Lectures for publication. Much new material had appeared since 1948, and considerable advances in theory had been made. The unifying concept for

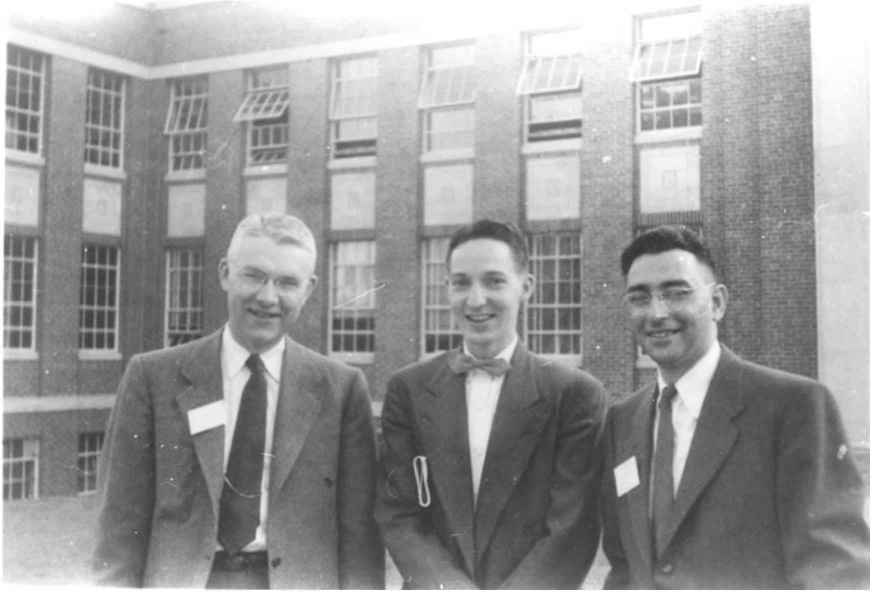


Fig. 2.7 Paul Flory, William Krigbaum and Leo Mandelkern at Cornell (James Mark, by permission)

the book is stated clearly in the Preface: "The author has been guided in his choice of material by a primary concern with principles." Hence the title: "Principles of Polymer Chemistry" [33]. While the scope of the book is vast, especially for 1953, Flory was careful to note that "it would scarcely be possible in a single volume to do justice to all the excellent researches in various branches of the subject." The fact that in 2014 it is still the central reference monograph in polymer science testifies to its importance. All of the issues raised in the preceding paragraphs are treated in detail in the book, and a uniform notation and point of view is adopted. This consistency and uniformity is one of the great strengths of the work.

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