THE FRACTIONATION OF HIGH-POLYMERIC SUBSTANCES[1]

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Received August 2, 1945

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[1] Financial support was received from the Associate Committee on Synthetic Rubber Research of the National Research Council of Canada.

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I. INTRODUCTION

A. GENERAL

A polymer is a compound[3] each molecule of which is formed (except for end groups) of a given number of structural units closely related to the molecules of the monomer (or monomers) from which the polymer is derived. It has, therefore, like other covalent compounds, a molecular weight; if its molecular weight is very large, it is a "high" polymer. Many high-polymeric substances are known, and as a class they are of great and increasing importance; yet high polymers in pure form are not known. Both the natural and synthetic high-polymeric substances are mixtures (2, 11, 18, 70, 177, 268); individual molecules may differ in size (i.e., in the number of repeating units, or, as it is often called, the degree of polymerization), in shape (i.e., in the degree of branching or cross-linking), and even in chemical composition (as, for example, in the case of nitrated cellulose). The important names in high-polymer chemistry, such as "cellulose", do not refer as in classical chemistry to pure chemical compounds; rather they are generic, denoting mixtures of compounds whose molecules, though very similar, may differ in size, shape, and composition. It is understandable therefore why the term "high polymer" has come to have a similarly generic meaning and why in general usage it signifies a high-polymeric substance rather than a high-polymeric compound. As this usage, although a bit confusing, is both common and convenient, it will be adopted frequently in this review.

High-polymeric systems may, however, be homogeneous in all respects but molecular size. Staudinger (17) has introduced the term "homologous polymeric series" for a series of linear (unbranched) polymers whose members differ in degree of polymerization but not in chemical composition. Many high-polymeric substances are found to be mixtures of members of such homologous polymeric series.

The fact that high polymers are heterogeneous is of tremendous importance; to their very heterogeneity they owe many of the properties that make them so interesting and useful. But it is important to realize that, being non-uniform, they are infinitely variable. The molecular-weight distribution of a high polymer, for example, may vary from sample to sample; with natural products it depends on the source of the material, with synthetics on the method of preparation, and with both on previous treatment such as purification, bleaching (of cellulose), or milling (of rubber). Therefore, in the interpretation and use of a measured value of any property that is a function of molecular weight, such as osmotic pressure or solution viscosity, it must be clearly recognized (*1*) that two samples giving the same value may yet be very different in other respects because of a different molecular-size distribution and (*2*) that a "molecular weight" cal-

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[3] NED defines "polymer" as (in part)" . . . any one of a series of polymeric compounds"; Webster's *New International Dictionary* (2nd edition, unabridged) defines it as " . . . any of two or more polymeric compounds."

culated from such a value will be merely an average value. Indeed, as Kraemer (150) (as well as others) has pointed out, the average molecular weight deduced from osmotic-pressure data is different from that deduced from viscosity data, because these properties are different functions of the molecular distribution. As many of the industrially important properties of high polymers likewise depend on the shape of the distribution curve, it is highly important that methods be available (*1*) for determining the molecular-weight distribution in the heterogeneous material without necessarily separating it into homogeneous fractions, and (*2*) for preparing fractions at least approaching homogeneity with respect to molecular weight, in order to make it possible to determine the true relation between a given property and molecular weight. Such fractionation methods, fortunately, have been and are being developed; the first type will hereafter be called analytical, the second (with which this review is primarily concerned) will be called preparative.

B. HISTORICAL

The idea that high-polymeric materials might be heterogeneous is not new. As far back as 1887 (79), 1888 (106), and 1900 (295, 296), natural rubber was believed to consist of two compounds, one soluble and one insoluble in organic solvents such as chloroform or carbon disulfide. (Later, ethyl ether (84) and petroleum ether (51, 84) were found more suitable for separating the two fractions.) Thus the earliest fractionation method was an extraction.

Fractional precipitation, which is now the most widely used fractionation method, was at first used for the purpose of purification (of rubber, by Caspari (51) in 1913) and only later for the separation of fractions (from nitrocellulose by Duclaux and Wollman (74) in 1920). It quickly became popular in the cellulose field, and was adapted to balata (271) and to various synthetic polymers (267, 269, 272, 273, 275–277, 280, 281) by Staudinger and his coworkers, beginning in 1927, and to rubber by Midgley and his associates (189) in 1931.

Fractional solution methods, although claimed by some to be superior to precipitation, have never come into such wide use. They were introduced by Craik and Miles (57) in 1931 and have been carefully studied in more recent years by Bloomfield and Farmer (39), Kemp and Peters (141), and others.

Other methods such as those involving ultracentrifugation or chromatographic adsorption have been used, but they are of much less general applicability. The ultracentrifuge has been shown (148, 150, 257, 258) to be well suited to analytical determination of heterogeneity, but cost and complexity have limited its use.

On the whole, there has been a steadily increasing recognition of the importance of fractionation both in research and for industrial control. Fractionation is an essential preliminary step in the application of viscosity measurements to the determination of the average molecular weight of a high-polymeric material; it makes possible the correlation of other physical properties with the average molecular weight and with the molecular-weight distribution; and it is indispensable in research on the kinetics of polymerization and depolymerization.

The growing interest in fractionation is evidenced by the increase in the number of papers published, dealing with fractionation, from three in the period 1920–24 to at least sixty in the period 1935–39.[4]

Reports of research studies involving methods for the fractionation of high-polymeric substances are scattered through many journals of various types, and often appear in papers devoted in large part to other matters. In this survey an effort has been made to collect and systematize such information concerning fractionation methods as has appeared in the literature to the end of 1944.

II. FRACTIONATION METHODS

In a discussion of fractionation methods classification is essential, but the classification might be based on any one of several considerations: the purpose of the fractionation,[5] the material fractionated, the principle underlying the method of separation. For the convenience both of those interested in the general subject of fractionation and of those more concerned with its application to a given type of high-polymeric system, the methods have been classified here on the basis of the separation principle, each class being further subdivided according to the material to which the method is applied.

METHOD	PRINCIPLE ON WHICH SEPARATION IS BASED
I. Solubility methods	Solubility decreases with molecular weight
1. Fractional precipitation	
(a) By addition of precipitant	
(b) By cooling	
2. Fractional solution	
(a) Solvent of varying composition	
(b) Varying temperature	
3. Distribution between two immiscible solvents	Distribution coefficient depends on molecular weight
II. Rate-of-solution method (diffusion into a single solvent)	Smaller molecules diffuse faster
III. Ultracentrifuge	Sedimentation velocity increases with molecular weight
IV. Chromatographic adsorption	Smaller molecules are preferentially adsorbed
V. Ultrafiltration through graded membranes	Sieving action
VI. Molecular distillation	Larger molecules are less volatile

A. Solubility methods

The solubility methods for fractionating heterogeneous high-polymeric substances depend on the greater solubility in a given liquid of the lower-mole-

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[4] It need hardly be mentioned that the number of papers published during the war years is no index of the recent activity in this field.

[5] The distinction between preparative and analytical methods, for example, has already been mentioned.

cular-weight species, and on the fact that the solvent power of a binary liquid mixture (of solvent and non-solvent) depends on the proportion of the two liquid components. If a non-solvent (also often called the precipitant) is added to a polymer–solvent system, as in fractional precipitation, or a polymer is added to a solvent–non-solvent mixture, as in fractional solution, two phases are obtained at equilibrium, if the proportions of the components are properly adjusted. The upper layer is a solution in which polymer is present in low concentration; the lower layer, or "precipitated" phase, is either a swollen gel or a very viscous liquid, and contains a high proportion of polymer. The material of higher molecular weight tends to concentrate in the precipitated phase, that of lower molecular weight in the supernatant liquid.

One of the earliest theories of solubility fractionation[6] was that of Brønsted (42). He suggested that when we consider only the members of a single homologous polymeric series the potential energy of the polymer molecules is proportional to the molecular weight, and the distribution of the molecules between the two phases is determined by a difference of potential energy, the less mobile large molecules collecting in the phase with the lower potential energy (the precipitated phase), the smaller and more mobile ones in the supernatant liquid. He derived the equation

$$\ln \frac{c'}{c''} = \lambda M/RT$$

where c' and c'' are the concentrations of polymer in the two phases at equilibrium, M is the molecular weight of polymer, and λ is a constant characteristic of the polymer–solvent system but independent of M.

Schulz (244, 246, 253) developed these ideas further by assuming that in the case of binary liquid mixtures λ is a linear function of the liquid composition and showed that the equation

$$\gamma^* = A + B/M \tag{2}$$

adequately expresses the relation between γ^*, the "critical" liquid composition at the precipitation point, and the molecular weight, M, of the polymer; A and B are empirical constants. He also applied the theory to heterogeneous polymers, using a rather arbitrary modification of equation 1, and concluded that the efficiency of fractionation is improved by keeping the concentration of polymer in the supernatant phase as low as possible.

The Brønsted–Schulz theory was remarkably successful in predicting the solubility behavior of high-polymer solutions. However, it was soon suspected that the entropy of mixing of polymer and solvent molecules was a factor of importance and should not be neglected in developing the theory of solubility.

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[6] In his report on "The Physical Chemistry of Rubber Solutions" Gee (100) has ably and critically reviewed contributions to the theory of the solubility and fractionation of high polymers up to 1943. See also his somewhat later review, "The Thermodynamic Study of Rubber Solutions and Gels," in *Advances in Colloid Science*, Vol. II, H. Mark and G. S. Whitby (*Editors*), pp. 145–95. Interscience Publishers, Inc., New York (1946).

Polymer molecules, in general flexible rather than rigid (8), should be capable of assuming a greater number of random configurations in solution than in the solid state (9), and longer molecules a greater number than shorter ones. Mark (7) assumed that although the decrease in solubility with increasing molecular weight is due principally to the increase in heat of solution, the increase in entropy on solution should make this decrease in solubility less rapid than would be expected if the heat of solution were the only factor. Furthermore, this entropy effect should become more important as the chain length increases. Gee and Treloar (104) measured the free energies and heats of solution and dilution for the system rubber-benzene, and from these values calculated the entropies of solution and dilution. The entropy of solution so determined was, as expected, very much greater than the ideal value. From the results of this investigation, Gee and Treloar concluded that "the main factor governing the solution of rubber is the abnormally large entropy of solution", a factor that had been completely neglected by Brønsted and Schulz.

An explanation for the anomalously large entropy of mixing had already been proposed by Meyer (185). He suggested that the deviation is due not only to the flexibility of the polymer molecules but also to the vast differences in size of the solvent and solute molecules (in the statistical calculation of the number of possible configuration of the system, we cannot imagine one solvent molecule replacing one solute molecule, as we do in solutions of substances with molecular weights of the same order of magnitude). As a model for a solution of a high polymer in a low-molecular liquid he proposed a lattice of $N_1 + nN_2$ sites, to be occupied by N_1 solvent molecules and N_2 polymer molecules, each of the latter consisting of n submolecules of a size comparable to that of molecules of solvent. Using this model, Flory (88, 89) and Huggins (121, 122, 123),[7] independently of each other, calculated the entropy of mixing and the activities of the components of a high-polymer solution. In outline, their argument is somewhat as follows: First, the number of different ways, ϕ, of placing the solvent molecules and polymer submolecules in the lattice are calculated, assuming for the moment complete flexibility at each junction between submolecules (this involves the assumption of unrestricted rotation around carbon–carbon single bonds), and neglecting certain minor complicating factors, such as crossing of the chains. Then, by the use of Boltzmann's equation

$$S = k \ln \phi \tag{3}$$

the entropy of solution of each component can be found. Assuming the heat of solution to be given by a Scatchard-Hildebrand formula

$$\bar{H}_1 - H_1^0 = kV_1\boldsymbol{v}_2^2 \tag{4}$$

($\bar{H}_1$ is the partial molar heat content of solvent in the solution, H_1^0 the molar heat content of pure solvent, K an empirical constant, V_1 the molar volume of

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[7] See also 5, 124, 125, and the more recent summary (Polymer Bull. **1,** 25–30 (1945)).

solvent, and $\mathbf{V}_2$ the volume fraction of polymer in the solution), the free energy of solution can be found, and from it the activity; for

$$(\bar{H}_1 - H_1^0) - T(\bar{S}_1 - S_1^0) = \bar{F}_1 - F_1^0 = RT \ln a_1 \qquad (5)$$

The equation finally derived is, in Huggins' notation,

$$\ln a_1 = \ln V_1 + (1 - \bar{V}_1/\bar{V}_2)\mathbf{V}_2 + \mu\mathbf{V}_2^2 + \text{higher powers of } \mathbf{V}_2 \qquad (6)$$

where $\bar{V}_1$ and $\bar{V}_2$ are the partial molar volumes of solvent and polymer, and μ is a constant characteristic of the polymer-solvent system, but independent of M, the molecular weight of the polymer. The terms containing higher powers of $\mathbf{V}_2$ are usually negligible. This equation gives the activity of the solvent at a given composition of the solution if $\bar{V}_1/\bar{V}_2$ and μ are known.

Now

$$\bar{V}_1/\bar{V}_2 = V_1\mathrm{d}/M \qquad (7)$$

(assuming the partial molar volumes to be equal to the molar volumes of the pure components), where V_1 is the molar volume of the solvent, and d is the density of the polymer, assumed to be independent of M. The quantity $\bar{V}_1/\bar{V}_2$ is therefore a measure of the molecular weight of the polymer, and Huggins' equation (equation 6) should give us information, regarding the dependence of solubility (expressed as $\mathbf{V}_2$) on molecular weight, necessary to the understanding of fractionation.

The constant μ is of no less importance, for its value depends on the liquid used with a given polymer, and will therefore vary as the composition of the binary mixture is changed during fractionation. Huggins has discussed in some detail (127) the factors that might be expected to affect the value μ: heat of mixing, the flexibility of the chain molecule, the molecular weight of the polymer, the concentration of the solution, the temperature, etc. Like Gee (100, 104), he relates the heat of mixing, which is an important factor in determining μ, to the "cohesive energy densities" of the polymer and the liquid (where cohesive energy density is, following Hildebrand (4), defined as the ratio of the molar latent heat of vaporization at constant volume to the molar volume), the heat of mixing being larger the greater the difference between these cohesive energy densities (100). If the difference is very great, the entropy of mixing is also affected, for then perfect randomness of mixing can no longer obtain. The result is that the entropy of mixing will be smaller than otherwise expected and the value of μ correspondingly larger.[8]

The effect on the entropy of mixing, and therefore on μ, of variation in flexibility of the chains is very slight; "a large decrease in flexibility makes μ slightly smaller in magnitude, if positive, or larger, if negative" (127). The contributions of both the heat and the entropy of mixing to μ should be smaller at higher temperatures because of the increasing probability of perfect mixing and the

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[8] The intrinsic viscosity $[\eta]$ of a polymer in a "poor" solvent (that is, one in which the heat of mixing is large) is less than that in a "good" solvent, a fact explained by assuming that the polymer molecules are more tightly coiled in the poor solvent (26, 89, 126).

increasing flexibility of the chain molecules. In practice, μ is found to vary with temperature according to the equation

$$\mu = \alpha + \beta/T \tag{8}$$

where α and β are constants. (This dependence of μ on temperature is the basis of another method of fractionation, for we can obviously increase μ, and thereby effect separation into two phases, by cooling as well as by addition of non-solvent.) μ is found to be almost independent of the molecular weight of the polymer and of the concentration of polymer in the solution (for a few systems it increases at high concentrations, but for the rubber–benzene system, for example, it is constant over the entire concentration range (127)).

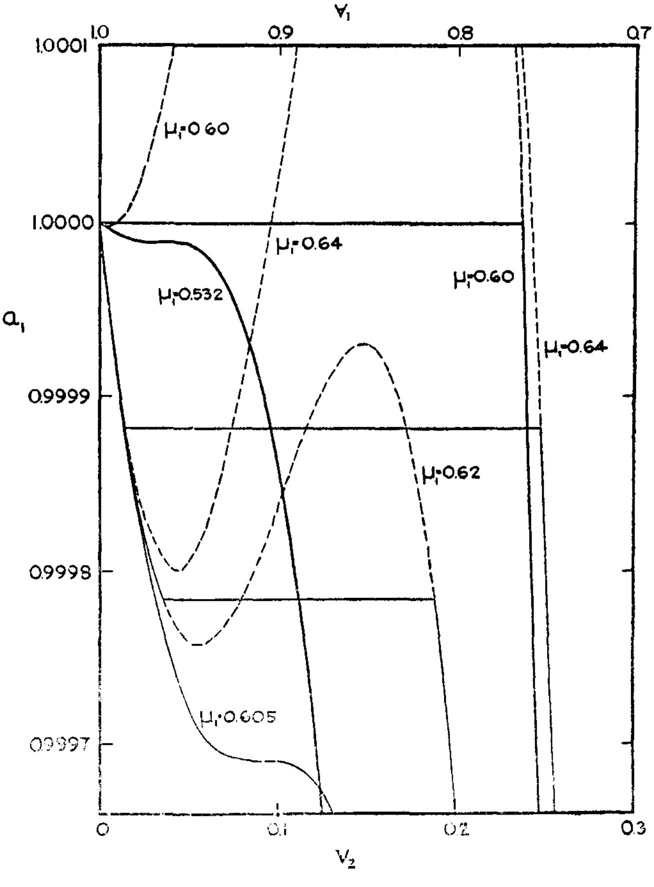

FIG. 1. Activity (a_1) vs. volume fraction for $\overline{V}_2/\overline{V}_1 = 100$ (lighter lines) and 1000 (heavier lines) at different values of μ (or μ_1). (From Huggins (5, p. 903)).

The significance of μ for fractionation is probably best demonstrated by plotting the activity, a_1, against the volume fraction $\mathbf{V}_2$ for various values of μ, keeping M constant (5, 127) (see figure 1). It is seen that when μ is below a critical value, the plot is a smoothly descending curve, and the polymer of this particular molecular weight is completely miscible in all proportions with the liquid; but when μ exceeds this critical value the curve shows a maximum and a minimum, indicating the presence of two phases. The shape of these curves shows that, in the region of partial miscibility, the liquid is much more soluble in the polymer than the polymer is in the liquid; one phase (the supernatant liquid) is almost pure solvent, while the other (the precipitated phase) is a more or less swollen polymer. The critical value of μ depends on M, as follows:

$$\mu_c = \tfrac{1}{2}(1 + \sqrt{\bar{V}_1/\bar{V}_2})^2 \tag{9}$$

so that as M becomes very large, μ_c approaches the value 0.5. Since in the high-molecular-weight range the values of μ_c are therefore very close together, fractionation will become correspondingly more difficult, and overlapping of molecular weights in the fractions more serious, in this range; this is the same conclusion as was reached by Mark (7) on the basis of a different theory, and it is in accordance with observed behavior.[9]

Gee (99) treated the problem of the solubility of a polymer (rubber) in a liquid in a similar way, except that in place of equation 4 he used a more complex expression for the heat of mixing. From his analysis it may be concluded (*1*) that for any liquid–polymer system there is a critical temperature above which complete miscibility obtains, this temperature being nearly independent of the molecular weight of rubber unless this be small; (*2*) that in the range of partial miscibility the concentration of polymer in the supernatant phase increases very rapidly with temperature (so that the temperature range in which a solubility is measurable is narrow), the coefficient increasing somewhat with temperature; and (*3*) that the composition of the precipitated phase depends only slightly on the molecular weight of the polymer.

In applying these theories to the fractionation of a heterogeneous polymeric substance, one should consider the possible effects on the solubility of a given polymer species of the presence in the same solution of other polymer species differing only slightly in molecular weight. Gee (99, 100), recognizing this need, used for the heat of mixing of such a polymeric substance an empirical extension of Flory's (89) equation for the entropy of mixing of long and short molecules (polymer and solvent), in the form

$$\Delta S_{\text{mix}} = -k(n_0 \ln \mathbf{V}_0 + \Sigma n_i \ln \mathbf{V}_i) \tag{10}$$

(where n_0 is the number of solvent molecules, n_i is the number of molecules of polymer species i, $\mathbf{V}_0$ and $\mathbf{V}_i$ are volume fractions, and k is the Boltzmann constant); and with this expression derived an equation relating the distribution of

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[9] Implicit in this discussion is the assumption that the relations are still applicable when the (homogeneous) polymer is mixed with others in a heterogeneous polymeric substance. That this assumption is valid, provided the molecular weight of the homogeneous polymer is replaced by the number-average molecular weight of the heterogeneous material, has recently been demonstrated theoretically by Scott (J. Chem. Phys. **13**, 178–87 (1945)).

the two species i and j between the two phases. His analysis led to the conclusions that fractionation is more efficient the more dilute the solution and that no single-stage fractionation by any solubility method can give anything approaching complete separation. The first of these conclusions had already been reached by Schulz (246, 247, 253); both are borne out in practice.

Flory (91, 92), in a much more thorough treatment of the problem, gave a theoretical derivation of equation 10 and from it derived expressions for the partial molal entropies and free energies of solvent and polymer. He pointed out that as a result of simplifying assumptions embodied in the theory the theoretical values of the entropies did not agree well with experimental values, especially in dilute solutions, but that the free-energy values calculated from them did agree well with experiment if μ, which occurs in the free-energy expressions, were considered a semi-empirical function. (Compare Huggins' discussion of the same function, above). Applying these equations to the problem of the fractionation of a heterogeneous polymer, Flory (92) developed an equation relating the "partition factor" α (which is defined as $\frac{1}{x} \ln(\mathbf{v}'_x/\mathbf{v}_x)$, where x is the degree of polymerization of molecular species x, and $\mathbf{v}'_x$ and $\mathbf{v}_x$ are the volume fractions of this species in the precipitated and supernatant phases, respectively) to μ, to the concentrations of (total) polymer in the two phases, and to the number-average molecular weights of the polymers in the two phases. He showed that the conditions of fractionation depend both on α, which governs the relative concentrations of a species in the two phases, and on r (the ratio of the volume of precipitated and supernatant phases), which affects the relative amounts. The nature of α is such that the concentration of any species, even that of lowest molecular weight, is greater in the precipitate than in the supernatant solution, although the concentrations become more nearly equal the lower the molecular weight. In order to reduce contamination of the precipitate with lower-molecular-weight material to a minimum, it is necessary that r be made very small, that is, that the volume of the supernatant solution be very large relative to that of the precipitate. The original solution should therefore be very dilute. This conclusion is in agreement with the familiar observation that fractionation is more efficient the more dilute the original solution. Flory was also able to show that the importance of using dilute solutions becomes greater as the molecular weight at which separation takes place increases.

The theory to this point has been developed on the assumption that the solvent is a simple liquid, or, if a binary solvent–non-solvent mixture, can be treated as one whose properties are intermediate between those of the solvent and the non-solvent. Gee (102) derived equations for the osmotic equilibrium between such a binary mixture and a ternary mixture of polymer and the liquid mixture, the two being separated by a membrane permeable to the two liquids but impermeable to the polymer, and then applied the equations to the solubility of linear polymer in mixed liquids. He was able to show that mixed liquids do not in general behave as simple liquids, that the larger the heat of mixing of two liquids the greater is the solvent power of the mixed liquid relative to that which would be expected if the properties of the two liquids were additive. He showed further how the solubility behavior of a polymer could be predicted "qualitatively from the cohesive energy densities of the three components, and semiquantitatively from the measured heats of mixing of the three binary mixtures." He also found that the distribution of the liquids between the two phases was unequal, the precipitate being richer in the better solvent.

It must be remembered that certain assumptions only approximately valid have been made in developing the theory of fractionation and that perfect agreement between theory and experiment can therefore not be expected (92, 99, 100). Nevertheless, the repeated experimental verification of many of the conclusions reached is evidence that the reasoning is basically sound. Further development of the theory is inevitable, and will undoubtedly throw further light on the process of fractionation.

The conclusions drawn from theory and supported by experiment have proven reliable guides in carrying out fractionation. In general it may be said that certain principles are well established. Fractionation is never completely efficient; the fractions obtained are never completely homogeneous with respect to molecular weight (72, 92, 149, 158, 263), although more nearly so than the original material. Refractionation improves the uniformity of the fractions, but only up to a certain point; there is no further significant improvement after the third fractionation (263). Better results are obtained by suitably recombining a large number of small fractions, if only a few are required, than by separating out the few larger fractions directly. The efficiency of a fractionation is greater the more dilute the supernatant solution (38, 176, 293),[10] and it is greater in the lower than in the high molecular-weight range (92, 127). This behavior is well shown by an isothermal ternary phase diagram (52, 92, 176, 263), such as is drawn in figure 2 for the generalized system: polymer-solvent-nonsolvent. In the diagram, which of course has no quantitative significance, the separation of the curves for the different molecular species is greater at low polymer concentration, and, at a given concentration, greater in the lower-molecular-weight range.

1. *Fractional precipitation*

Fractional precipitation procedures are those in which the heterogeneous polymer is completely dissolved in a suitable liquid and then partially "precipitated". The precipitated phase, which contains the high-molecular-weight fraction, and the supernatant solution are separated by decantation (with or without centrifuging); more of the polymer is then precipitated, and the procedure is repeated. There are two principal ways in which precipitation can be effected, and these will be considered separately: (*a*) by adding a precipitant isothermally; (*b*) by lowering the temperature, keeping the total composition constant. A combination of the two can, of course, be used.

[10] See, however, the evidence to the contrary obtained in recent experiments by Morey and Tamblyn (J. Phys. Chem. **50**, 12–22 (1946)).

In an actual fractionation, the choice of solvent and precipitant is important. Relative solvent and precipitating powers can be determined by titrating a solution of the polymer in the solvent with the precipitant, the end point being indicated by the sudden appearance of opalescence or turbidity (25, 83, 138). Such a procedure is called a precipitation titration. The larger the amount of precipitant needed to reach the end point, the greater is the solvent power of the solvent (when one precipitant is used with a series of solvents), or the smaller is the precipitating power of the precipitant (when one solvent is used with a series of precipitants). The position of the end point depends on the polymer concentration (302), as an examination of the phase diagram (figure 2) shows. The results of a precipitation titration study are best summarized in such a phase diagram, and the diagram is a valuable help in carrying out fractionations.

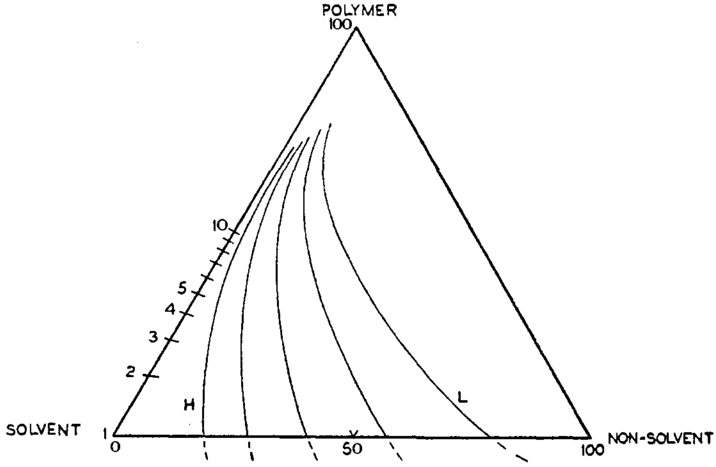

FIG. 2. General isothermal equilibrium diagram: polymer–solvent–non-solvent. H = highest molecular weight fraction; L = lowest molecular weight fraction. Adapted from H. Mark (Paper Trade J. **113**, 34–40 (1941)).

Theories as to why liquids differ in their solvent and precipitating power have not yet been completely formulated. Gee (103) showed that the solvent power of a binary liquid mixture is intermediate between that of the components only if they mix ideally; the larger the heat of mixing, the greater is the solvent power of the mixture relative to that of the components. Erbring (81) compared the precipitating power of the saturated monohydric alcohols from methyl to octyl (including some secondary ones) on the following systems: (*1*) polystyrene in each of ethyl acetate, butyl acetone, carbon tetrachloride, chloroform, methyl ethyl ketone, benzene, xylene, toluene, and monomeric styrene; (*2*) cellulose acetate in acetone; (*3*) paraffin in benzene; (*4*) rubber in each of benzene, carbon tetrachloride, and chloroform. In general, he found a relationship between precipitating power and dielectric molecular polarization of the alcohol; in (*2*) and in most cases in (*1*), there was a direct relationship; in (*3*) and (*4*) it was inverse; but with polystyrene in methyl ethyl ketone the precipitating power was virtually independent of the molecular polarization. Since the molecular polarization increases with the molecular weight of the alcohol, this means that the higher alcohols are more effective than the lower ones in precipitating cellulose acetate (which contains polar groups), but less effective in precipitating the non-polar substances paraffin and rubber. In later work, polystyrene (82), polyvinyl chloride (80), and polyisobutylene (80) were found to behave like paraffin and rubber in this respect. Polymethacrylic esters (80) behaved like cellulose acetate; with benzyl cellulose (80) a maximum precipitating power is shown by hexanol. Even more significant than its correlation with molecular polarization is the relationship of precipitating power to the quantity μ^2/ϵ where μ is here the dipole moment and ϵ the dielectric constant; this relationship is approximately linear in many cases (80, 82). Similar studies have been made by several other workers (105, 146, 175, 286, 303).

It is obvious that the end point of a precipitation titration may be located by observing the sudden increase in turbidity, either directly (138) or instrumentally (25, 83, 105, 195, 233). Gehman and Field (105), for example, observed that if light-scattering measurements are made as precipitant is slowly added, the intensity begins to increase long before two phases separate, but that there is a very marked increase of intensity at the precipitation point. They attributed the earlier increase in turbidity to aggregation of the molecules into loose clusters. The precipitation point may also be detected by measuring the depolarization of scattered light (105), the surface tension (174), or the viscosity, during the titration. Viscosity measurements, in particular, have frequently been used for this purpose (119, 153, 174, 224, 233). The marked decrease in the viscosity of a polymer solution on the addition of a non-solvent is a familiar phenomenon; several explanations for it have been advanced (105, 110, 276), but it is probably best explained as due to the tighter curling and more compact shape of the polymer molecules in the "poorer" solvent medium (26, 126). As more non-solvent is added the viscosity decreases less rapidly (105) (and may become constant (110) or even increase slightly (153)); the sudden decrease in viscosity when precipitation begins therefore produces a sharp break in the "viscometric titration" curve at the end point (see, for example, figure 3).

Precipitation titration can be used to determine the molecular weight of a polymer in a solution (the weight-average molecular weight in the case of a heterogeneous polymeric substance). This method, like that involving the determination of intrinsic viscosity, is a relative one, and must be calibrated using one of the absolute methods (ultracentrifuge, osmotic pressure, light scattering). The Schulz equation (equation 2), which is valid for a wide variety of polymeric substances, may be used for this purpose in the form $\lambda^* = A + B/\bar{M}$. It is obvious from this equation that the sensitivity of the method decreases with increasing molecular weight. This method was applied by Schulz and Dinglinger to polymethyl methacrylates (250), by Staudinger to polystyrene (274), by Jirgensons to degradation products of proteins (131–137), by Adams and Powers to varnish resins (25), by Baker, Fuller, and Heiss to ω-hydroxyundecanoic self-polyesters (30), by Husemann to degraded glycogen (129), and by Lovell and Hibbert to polyoxyethylene glycols (168). It is a promising new method, attractive because of its simplicity.

(a) Fractional precipitation by the addition of a precipitant

In this method fractionation is effected by adding to a solution of the polymer a suitable amount of precipitant, enough to cause separation into two phases, but not enough to cause precipitation of all the polymer present; the phases are then separated, and the procedure repeated with the supernatant liquid, until all the polymer has been precipitated (material of very low molecular weight may remain in solution even when excess precipitant has been added, but the amount is usually not large). In a preparative method, the fractions are recovered from the precipitated phase by evaporation of the solvent and drying; in an analytical method, it is usual to determine the amount of unprecipitated polymer in the supernatant liquid by evaporating an aliquot sample. Various modifications of these fundamental procedures are possible; these will be discussed as the individual fractionation procedures are considered.

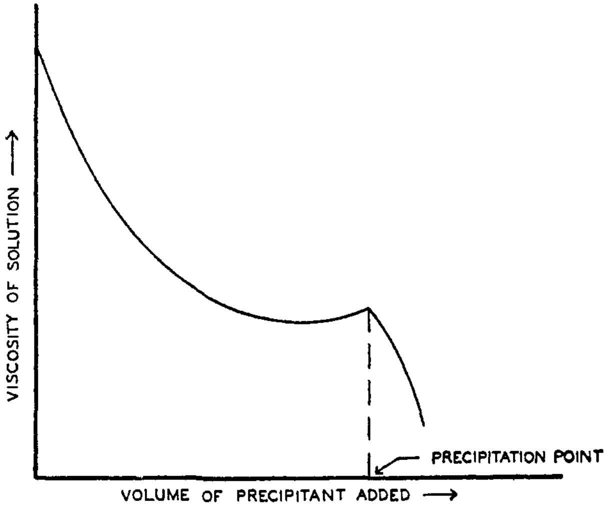

FIG. 3. A viscometric precipitation titration curve

(*1*) *Rubber and other natural hydrocarbons:* Caspari in 1913 (51), in a discussion of the fractionation of rubber into sol and gel by diffusion, expressed the opinion that a separation by fractional precipitation with alcohol or acetone would not be possible. Again in 1915 (52), on the basis of phase studies of the systems rubber-benzene–alcohol and rubber-benzene–acetone, he concluded that even if rubber were heterogeneous, fractional precipitation would not be feasible.

In spite of his conclusions, fractional precipitation was used successfully by Pummerer and Koch (218) in 1924 for the purpose of purification of rubber. These authors precipitated rubber from a 3 per cent solution in benzene by adding a 1:1 benzene–alcohol solution (in an atmosphere of carbon dioxide to exclude air and prevent degradation). They found that the impurities were removed with the first fraction. This procedure was further studied by Pummerer and Miedel in 1927 (219); it was found that when just enough precipitant was added to produce permanent turbidity, the first fraction contained 30–40 per cent of the total rubber hydrocarbon, together with all the impurities. The material remaining in solution was considered pure, since its elementary analysis corresponded to the theoretical formula. A study was also made of other solvents (hexahydrotoluene, petroleum ether, ethyl ether) and other precipitants (acetone) for use in the process. The best control of the conditions of precipitation was achieved with petroleum ether as solvent and acetone as precipitant. In some cases there was some doubt about the purity of the product, for traces of nitrogen were found to be still present. In 1928 the same authors (220) critically compared the various purification procedures in use at that time. The fractional precipitation technique was improved by repeating the precipitation and by varying the solvents, precipitants, concentration, and temperature; in the hope of achieving a more thorough purification, a different solvent-precipitant system was used in each refractionation. Eight fractions were obtained in this way, but the authors were still not satisfied with the purity of their products.

In 1939 Kovarskaya and Lipatov (147) fractionated pale crepe rubber by precipitation with ethanol from solution in either ethyl ether or benzene; six fractions were obtained, and used in a viscosity study.

In 1941, Kemp and Peters (141) compared various fractionation methods: diffusion into a single solvent, solution in mixed solvents of varying composition, precipitation by cooling, and finally a combined diffusion and precipitation method. This last procedure, which they considered the best, was as follows: 2.5 g. of finely cut crepe rubber was left to diffuse into 500 cc. of chloroform for definite periods of time at 25°C., and the resulting solution then fractionally precipitated with methanol. The residue was covered with 500 cc. of fresh chloroform, and the procedure repeated three times. Throughout, the work was carried out under an atmosphere of nitrogen. The separation was good, and no breakdown occurred.

In 1930, Staudinger (280) reported a fractional precipitation procedure for hydrorubber, a derivative of rubber produced by complete hydrogenation. He obtained five fractions by precipitating the ether solutions with alcohol.

(*2*) *Cellulose nitrate:* A great deal of work has been done on the fractionation of the cellulose esters, especially the nitrates and the acetates. This is not only because the esters themselves are of great industrial importance, but also because the best way to determine the distribution of cellulose itself is to nitrate or acetylate it carefully under such conditions that breakdown is minimized, and then fractionate the esters. The fractionation of cellulose itself has been carried out, and examples will be given later; but it presents considerable difficulties for cellulose does not dissolve in any simple solvent, and any liquid that does act as a solvent usually causes some breakdown (15).

The first paper to be published on fractional precipitation dealt with nitrocellulose; in it, Duclaux and Wollman (74), in 1920, introduced the method, which is still the standard and most widely used one, of precipitating an acetone solution with water, or with a water–acetone solution. One hundred and ten grams of commercial nitrocellulose was dissolved in 2 liters of acetone; with continual stirring, 1400 cc. of an acetone–water solution (60 per cent acetone by volume) was added; this gave, after separation and evaporation, the first fraction (42 g.). To the supernatant liquid 1 liter of 20 per cent acetone solution was added, and a second fraction (47 g.) precipitated. Then an excess of water was added, and the third fraction (16 g.) was obtained. Each of the fractions was fractionated in turn, but found to be still heterogeneous. By comparing properties of the fractions, it was found that they differed in viscosity (and therefore in molecular weight), but not in nitrogen content.

This method was adapted by Bréguet (41) in 1925 for use with celluloid, by using benzene as the precipitant instead of water in order to prevent the precipitation of the camphor.

In 1928, Kumichel (153) first described the technique of locating the precipitation point viscometrically. He found that on adding a 1:1 acetone–water solution to an acetone solution of nitrocellulose, the viscosity first fell, then increased again to a sharp point, at which turbidity appeared; a few more drops made the viscosity fall to a very low value, and precipitation occurred (see figure 3). After separation, two fractions were obtained by drying the precipitate and ultrafiltering the supernatant liquid. By a repetition of this procedure, the uniformity of the fractions could be improved.

Duclaux and Nodzu (73) in 1929 compared fractional precipitation with other fractionation methods involving diffusion and ultrafiltration. The earlier finding, that the fractions differ in molecular weight but not in the degree of nitration, was confirmed.

In 1930, Beck, Clément, and Rivière (35) carried out a fractional precipitation of a 16 per cent acetone solution of nitrocellulose by adding varying amounts of a 20 per cent water–80 per cent acetone mixture. As the last (fourth) fraction could not be precipitated with water, a barium chloride solution was used, but difficulty was experienced in washing out the barium chloride afterwards without peptizing the precipitate. A rather ingenious continuous procedure was described: a mixture of nitrocellulose, acetone, and water, in proportions such that precipitation did not occur, was distilled at reduced pressure at room temperature; as the acetone evaporated more rapidly than the water, a composition was soon reached at which precipitation began, and thereafter precipitation proceeded as the distillation continued. This method gave eleven fractions.

Duclaux and Barbière (72) in 1933 showed by successive fractionations that there is a limit beyond which the uniformity of a fraction cannot be significantly improved by further refractionation.

In 1933, Medvedev (182, 183) fractionated nitrocellulose, using acetone as the solvent and water as the precipitant. He introduced the practice of determining the amount of precipitant to be added by carrying out a preliminary titration of a small sample. He obtained nine fractions by suitable refractionations and compared their characteristics.

In 1934 and 1935, Glikman (Glückmann) (107, 108, 109, 111, 112) used Duclaux's fractional precipitation method in his study of the nature of nitrocellulose solutions. In some cases (109) solvents other than acetone were used (ethyl acetate, benzene). A fractionation by vacuum and ordinary distillation of a nitrocellulose-acetone-water mixture was also attempted (111). The fraction used by Dobry (63, 64) in her work on the viscosity and the osmotic pressure of nitrocellulose was obtained by precipitation, probably by Duclaux's method.

In 1935, Rogovin and Glazman (225) used the method to separate commercial nitrocellulose into three fractions, but unlike other investigators, they found a lower nitrogen content in the lowest fraction.

Schulz (243) in 1936 used a similar method but, realizing the importance of temperature control, carried out the separation after long standing (1-2 days) in the thermostat at 27°C.

Spurlin (264) in 1938 rejected water as a precipitant, because it produces a high Tyndall effect. Instead he used acetone as the solvent, with heptane as the precipitant. Six fractions were obtained in the first fractionation; fractions of approximately the same viscosity were combined, and refractionated. This was repeated twice, giving a total of sixty-six fractions, which were combined to give seventeen. A high degree of separation was attained, but not homogeneity. This is an important study, because of the large number of fractions and their relative uniformity; it made possible a valuable study of the correlation of mechanical properties with molecular weight.

Rath and Dolmetsch (223) in 1938, in a search for the best method of determining the heterogeneity of cellulose, tried among other things a fractional precipitation of the nitrated product from acetone solution with water or ethanol. Similarly, Staudinger and Jurisch (278), in 1939, fractionated cellulose nitrate by precipitation with water from solution in acetone.

In 1940, Jurisch (138) precipitated cellulose nitrate from acetone by titrating with water. He described carefully the appearance of the solution near the precipitation point, as this is somewhat difficult to recognize. The mixture was then centrifuged, and the supernatant solution decanted. The precipitate was washed out of the centrifuge tube with acetone, reprecipitated with methanol and water, dried, and weighed. Although some material was lost in this process, this was not considered important, for the loss did not come from any one fraction, and the results were therefore not distorted.

Schulz (252, 254) fractionated nitrocellulose in 1941 and 1942, but did not describe his method.

(*3*) *Cellulose acetate:* In his study of the viscosity of cellulose acetate solutions, in 1923, Mardles (172) mentioned that the fractions he used were obtained by precipitation with water from acetone solution, but gave no further details.

In 1928, Caille (46) described a fractionation procedure as follows: 10 g. of cellulose acetate was dissolved in 300 cc. of acetone, 100 ml. of acetone-water (1:1) solution was added with stirring, and the precipitate was washed and dried; the process was then repeated on the supernatant liquid.

McNally and Godbout (171) in 1929 precipitated a 10 per cent acetone solution fractionally with 3:1 water–acetone solution; the separation of phases was carried out by centrifuging.

In 1930 Rocha (224) applied the "viscometric titration" method of Kumichel to cellulose acetate. He obtained three fractions, the lowest of which contained most of the impurities, and characterized them very thoroughly by various chemical and physical tests. The fractional precipitation of cellulose acetate from acetone with water is often known as Rocha's method, although he did not originate it.

Ohl in 1930 (205) and 1932 (206) applied the same method and obtained three fractions, of which the second was the purest. A correlation was found between properties of fractions and the quality of products made from them; therefore, fractionation was suggested as a basis for judging the quality of cellulose acetate. The method was also used in 1931 by both Iwasaki (130) and Caille (47).

Herzog and Deripasko (119) in 1932 made a study of other solvent–precipitant systems for use in the fractionation of cellulose acetate; among them methyl glycol–water and acetone–petroleum ether. The precipitation point was determined viscometrically as by Rocha.

In 1934, a whole series of papers was published. Clément and Rivière (53), Obogi and Broda (203), and Herz (117) all used methods similar to those already described. Elöd and Schmid-Bielenberg (77) and Hess and Ulmann (120) used chloroform as the solvent and methanol as the precipitant. In 1935 Rocha's method was used by Ulmann (293), who emphasized that the solution should be dilute, but considered the 2.5 per cent solution he used dilute enough.

An important series of studies was made in 1937–39 by Lachs, Kronman, and Wajs (155, 156, 157, 158, 159). Their object was to find a method for determining the molecular-size distribution of cellulose; for that purpose, they acetylated it, and then precipitated the cellulose acetate fractionally from the final reaction mixture (1:1 acetic acid–acetone) with water. Usually four fractions were obtained. The general shape of the precipitation curve was noted: at first, the addition of large amounts of water produced little precipitate, then the further addition of small amounts caused heavy precipitation, and then the curve levelled off again, until no more precipitate could be obtained although some low-molecular-weight material was left in solution. It was confirmed that the fractions had the same acetyl content, but different viscosities. By successive acetylation, saponification, and reacetylation it was shown that little breakdown occurs in the process of acetylation. Cellulose from five different sources was used for this work. The degree of heterogeneity was measured roughly by the difference in viscosity of the first and last fractions. A second fractionation of the above fractions was then carried out, by precipitation with methanol from chloroform solution. It was shown that the first fractions were not homogeneous, but the estimate of the heterogeneity of the original cellulose was not greatly affected. An artificial mixture of two different fractions was fractionated, to prove the efficiency of the method.

In 1938, Levi *et al.* (164) used this method, with benzene as precipitant and acetone as solvent, as a standard against which to compare a fractionation (of cellulose acetate) by chromatographic adsorption.

Danilov *et al.* (59) in 1939 used fractional precipitation from acetone solution with ethyl ether as a means of purifying cellulose acetate. In the same year, Bezzi and Croatto (37) used a fractional precipitation involving the addition of water to an acetic acid solution. Mark and Simha (180) in 1940 applied Rocha's method on a larger scale, using 4 kg. of cellulose acetate.

A careful study of the fractional precipitation of cellulose acetate from acetone solution with ethanol was made by Sookne, Rutherford, Mark, and Harris (263) in 1942. To 150 liters of a 2.5 per cent solution of commercial cellulose acetate a quantity of ethanol insufficient to produce precipitation at room temperature was added, and the mixture cooled slowly to 10°C., where precipitation occurred. The phases were separated by decantation and the procedure repeated. The amount of ethanol to be added was determined in each case by a preliminary test-tube experiment. Three fractionations were done, fractions of closely similar mean-degree of polymerization being combined after each step; finally, fifteen fractions were obtained. The distribution curves plotted after each step show that refractionation results in improvement, but that no more improvement is possible after the third fractionation, although the fractions are still not homogeneous. These fractions were used in 1943 by Bartovics and Mark (31) in an osmometric and viscometric study.

(*4*) *Cellulose ethers and other derivatives:* Okamura (207) in 1933 fractionated technical ethyl cellulose by precipitation with water from glacial acetic acid solution. This solvent caused some breakdown, but not enough to matter.

Glikman (Glückmann) (110, 113) in 1936 and 1937 prepared fractions of benzyl cellulose, by precipitation with alcohol from an alcohol–benzene solution; they differed in molecular weight, but not in the degree of etherification. He also studied the temperature dependence of the precipitation, and the changes in the viscosity on addition of precipitant.

Signer and Liechti (259) in 1938 used a somewhat different method of fractionating a water-soluble methyl cellulose. To a 2.5 per cent aqueous solution of the technical material saturated sodium sulfate solution was added, and after separation of the precipitated phase the supernatant liquid was treated with solid sodium sulfate; fractions III and IV were also obtained with the use of the solid salt. (This "salting out" procedure is somewhat different in principle from the methods which use two liquids.) Fraction IV was refractionated, this time with acetone as the precipitant. The fractions had to be freed from sodium sulfate by dialysis or electrodialysis. Fractions differed not only in molecular weight, but also in methoxyl content.

Staudinger and Reinecke (279) in 1938 fractionated ethyl cellulose by precipitation with water from dioxane solution, obtaining three fractions of identical chemical composition.

In 1939 Ushakov *et al.* (294) described another method for fractionating ethyl cellulose, involving precipitation with gasoline from a 4 per cent alcohol solution.

They found that, in many cases, the fractions differed chemically as well as in molecular weight. The mechanical properties of the films obtained from the fractions were compared.

Fink, Stahn, and Matthes (85) in 1934 fractionated cellulose xanthogenate (viscose) by precipitation with methanol or ether from an aqueous pyridine solution. The fractions differed chemically as well as in chain length.

(*5*) *Cellulose:* As mentioned above, the direct fractionation of cellulose presents considerable difficulty (15), for cellulose does not dissolve in any simple solvent; the usual solvents, such as sodium hydroxide, phosphoric acid, or cuprammonium (Schweizer's reagent), all dissolve cellulose by chemical action, which is often drastic enough to cause appreciable breakdown, thus invalidating the results. Attempts have been made, however, to use all of these solvents, as well as others, for fractionation; for, in the more usual alternative procedures of nitrating or acetylating the cellulose and then fractionating, breakdown also occurs, during the esterification process. The choice is therefore one of two evils.[11]

In 1939, Tydén (291) brought cellulose into solution by digestion with zinc oxide and sodium hydroxide, and then precipitated it fractionally by "salting out" with sodium sulfate. It was found better to add the sodium sulfate in two portions, with a 3-hr. interval between additions, in order to obtain a smaller fraction; even then, 66 per cent of the cellulose precipitated. The concentration of the cellulose was about 0.1 per cent, and that of sodium sulfate 7–15 per cent; 12 hr. was required for complete flocculation. In this process, breakdown was minimized, but nevertheless did occur.

In 1942, Strauss and Levy (284) claimed that fractionation procedures for cellulose could be considerably improved by using their new solvent, cupriethylenediamine, which they had previously used successfully for viscosity measurements on cellulose; solutions of cellulose in this solvent are said to be less sensitive to breakdown than in others, especially by atmospheric oxygen. Cellulose, dissolved in 0.5 molar cupriethylenediamine solution to give a 1 per cent solution, was precipitated by titrating with 8 N sulfuric acid, with stirring, at 25°C.; the fractions were separated by centrifuging and decanting. Eight fractions were obtained by this procedure.

Further studies of fractional precipitation of cellulose were made in 1943 by Coppick, Battista, and Lytton (55). They decided in favor of an analytical rather than a preparative procedure, as this requires less time and less handling of the material, and thus minimizes degradation. In the actual method used, sodium hydroxide was the solvent, aqueous acetone the precipitant. In order to effect complete solution of the cellulose in the sodium hydroxide, the mixture was cooled slowly in an acetone–solid carbon dioxide bath with gentle stirring until solidification took place; then with vigorous stirring it was warmed up to

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[11] Indeed, for the fractionation of cellulose, a solution method is often preferable to precipitation, because it does not require the preliminary complete solution of the whole sample, a step which is sometimes impossible and often difficult, and which usually requires long periods of contact with the solvent, thereby increasing the chances for breakdown.

room temperature and the required quantity of aqueous acetone was added to it dropwise over a period of half an hour. The precipitate was separated by centrifuging and discarded. The amount of unprecipitated cellulose was then determined by adding acetic acid and methanol to an aliquot portion of the supernatant liquid at 0°C. until precipitation was complete, followed by washing, drying, and weighing the solid. Its cuprammonium viscosity was then determined to find the chain length needed for plotting the distribution curve. To obtain other fractions, the same amounts of different precipitation mixtures (20–50 per cent by volume of acetone) were added to fresh portions of the solution. (This is a typical analytical procedure; the fractions are never isolated at all, for the precipitates are discarded; the information obtained,—namely, the concentration of polymer remaining in solution after a known amount of precipitant has been added, and the viscosity of this polymer,—is sufficient to obtain a distribution curve, which is all that is required.) This method, useful for rayon, was adapted for use with wood pulp and cotton linters, which are only slightly soluble in sodium hydroxide. A special pretreatment, involving reprecipitation from cupriethylenediamine, was necessary to bring about complete solution in sodium hydroxide (6 *N*). Otherwise the procedure was similar.

(*6*) *Natural products other than rubber and cellulose:* Most of the proteins are neither linear in structure, nor heterogeneous in molecular weight (as Svedberg has shown with the ultracentrifuge). In this account, we are interested only in linear heterogeneous proteins, capable of forming a homologous polymeric series. Such a protein is gelatin. In 1926, Northrop and Kunitz (202) separated gelatin into two fractions by precipitation with alcohol from water, and compared the properties of the fractions. Nagorny (199) in 1927 accomplished the same end by fractional salting out with ammonium sulfate.

Among the carbohydrates other than cellulose, glycogen and starch have received some attention. Staudinger and Husemann (277) in 1937 fractionated glycogen by precipitation with methanol from formamide solution; comparative osmotic and viscosity measurements indicated, however, that the molecules are spherical rather than linear. In 1941, Husemann (129) used fractional precipitation to purify hydrolytically degraded glycogen; he separated it into three fractions by precipitation with methanol from 0.1 *N* calcium chloride solution, and discarded the first and last fractons. Levine, Foster, and Hixon (165) in 1942 applied a fractional precipitation procedure to crude dextrins obtained from corn syrup, precipitating with methanol from water solution; the fractions contained only from two to twenty-six glucose units per molecule, and were therefore not truly high-molecular.

Coppick and Jahn (56) in 1943 made a study of nitrated wood, and described a procedure for fractionating nitrated spruce mechanical pulp by slow precipitation from acetone with alcohol and water. Eight fractions were obtained.

(*7*) *Synthetic products:* Synthetic high polymers have increased remarkably in importance in the last few years; most of the fractionations reported are therefore comparatively recent. Nevertheless, Staudinger some time ago used synthetic polymers, such as polyethylene oxides and polystyrenes, as models in trying to elucidate the structure of the natural high polymers, and some early fractionation methods are due to him. In 1927 he (275) reported two methods for the fractionation of polyvinyl acetate, one by fractional solution, another by fractional precipitation; in the latter the addition of petroleum ether to a rather concentrated (40 per cent) benzene solution yielded three fractions. In 1929 he (273) reported a fractionation of polystyrene that is of special interest, because the precipitation was effected by an excess of solvent. The method was applied to the hemicolloidal (relatively low molecular weight) polystyrene: 170 g. of polymer was dissolved in 500 cc. of acetone; when 1000 cc. more of acetone was added, part of the polymer precipitated as a thick liquid. The process was repeated, and the last fraction, after partial evaporation of the acetone, was obtained by precipitation with alcohol. A refractionation from benzene solution was effected by the addition of a solution of benzene in alcohol. Five fractions were obtained in this way. In the same year, Staudinger and Schweitzer (281) obtained three fractions by the precipitation of polyethylene oxide with ether from benzene solution.

In 1928, Whitby and Katz (300) studied the polymerization of indene, cinnamalfluorene, and cinnamalindene. They demonstrated the heterogeneity of the products by fractional precipitation, using benzene as the solvent and alcohol as the precipitant; polyindene yielded seven fractions, polycinnamalfluorene five, and polycinnamalindene four. The same authors (299) reported another fractionation of polyindene in 1930, involving precipitation with alcohol from chloroform solution. Three fractions were obtained as follows: to a solution containing 450 g. of polyindene in 1200 cc. of chloroform, 200 cc. of alcohol was added dropwise with stirring. After separation of the first fraction, 1 liter of alcohol was added to the supernatant liquid to give the second fraction. The third fraction was obtained by concentrating the second supernatant liquid to 200 cc. The first fraction was subjected to nine refractionations, to remove the low-molecular-weight polymer.

In 1930, Whitby (297) described a fractional precipitation of polystyrene from benzene solution (1.5 per cent) with ethanol; three fractions were obtained. He also gave the results of a fractionation of polymerized dimethylbutadiene, without describing the method. In 1932 he (298) mentioned a similar fractionation of polystyrene in which he obtained six fractions.

A careful study of the fractionation of polystyrene, the most widely studied synthetic polymer, was made in 1934 by Daneš (58). He emphasized the temperature dependence of solubility, and the importance of close temperature control; he also used dilute solutions, to prevent the formation of emulsions, which are difficult to break. He employed the very useful technique of heating the mixture (after addition of precipitant) to not more than 20° above thermostat temperature until it formed a clear solution, and then letting it cool slowly, thereby ensuring conditions more favorable for the maintenance of equilibrium, and improving the homogeneity of the fractions. His solvent was benzene; his precipitant a mixture of methanol and acetone. Some of the fractions were refractionated.

Schulz and Husemann (251) in 1936 also fractionated polystyrene, using methyl ethyl ketone as the solvent and methanol as the precipitant. Temperature control was used, and seven fractions were obtained. In the same year, Dobry and Schwob (67) fractionated polystyrene by precipitation with methanol from various solvents: chloroform, benzene, tetralin, carbon disulfide, carbon tetrachloride, dioxane, pyridine. Two fractions only were obtained, for osmometric and viscometric study.

In 1936, Komarov and Selivanova (146) studied the conditions of the precipitation of sodium butadiene polymers from benzene solution by means of various alcohols and other liquids. They found that decrease in concentration and increase in temperature result in an increase in the amount of precipitant required. The chemical nature of the precipitant has a great influence on the position of the precipitation point; the series, in order of decreasing precipitating power, is: methanol, ethanol, phenol, propanol, acetone.

In 1936, Douglas and Stoops (71) used an analytical fractionation method to determine the distribution in vinyl ester resins. Measured amounts of precipitant (acetone-water solution) were added to a solution of the resin in acetone; a determination of total solid was made on a 10-cc. aliquot portion of the supernatant liquid; then, without separating the precipitate, more precipitant was added, and the procedure repeated. The considerable error was due to the overlapping of the molecular-weight ranges of the fractions.

Zhukov and Komarov (305) in 1938 reported the separation of sodium bivinyl polymer, by precipitation with alcohol from benzene solution, into four fractions. In the same paper an analytical procedure was also described in which varying amounts of alcohol were added to three portions of a 1 per cent benzene solution, and the precipitated fractions weighed.

In 1941, Schulz and Dinglinger (250) fractionated polymethyl methacrylates by successive additions of cyclohexane to benzene solutions. Blease and Tuckett (38) precipitated polyvinyl acetate from solution in acetone with 1:1 methanol-water solution; water was the actual precipitant, methanol acting merely as a diluent, to ensure easier control of the precipitation point; the control was also improved by precipitating at a higher temperature, because the quantity of precipitant to be added is then larger. It was found that a better separation was obtained in more dilute solution.

In the same year, Fuoss (95) described a procedure for the fractionation of polyvinyl chloride, using mesityl oxide as the solvent for low-molecular-weight products, cyclohexanone for high-molecular-weight products, acetone as a diluent, and methanol as the precipitant. Two methods were given, differing mainly in the quantities of materials used. The smaller-scale method (used more for analytical than for preparative purposes, although the fractions were actually separated) was as follows: 1 to 2 g. of polymer in a tared 200-cc. centrifuge bottle was moistened with acetone (for dilution improves the fractionation). Methanol was then added from a weight buret through a capillary funnel, in such a way that it mixed with acetone at indentations in the condenser, and was thus diluted without increasing the total volume of the solution. The solution was cooled slowly, then chilled in ice, and centrifuged; the supernatant liquid was decanted into another tared centrifuge bottle, and the procedure repeated. The precipitates were coagulated, filtered, dried, and weighed, and samples taken for viscosity determinations. In 1943, Fuoss and Mead (96) prepared polyvinyl chloride fractions by precipitating an acetone extract of the polymer with methanol.

In 1942, Staudinger *et al.* (270) reported a fractionation of polyisobutylene. The hemicolloidal products were precipitated with acetone from benzene solution, the mesocolloidal and eucolloidal products with acetone or methanol from toluene solution. Kern and Fernow (145) fractionated polymethacrylonitrile in 1942 by precipitation with methanol from a 1 per cent solution in acetone.

In 1943, Flory (90) fractionated polyisobutylene and used the fractions in a comparative viscosity-osmotic pressure study. He precipitated a 1 per cent benzene solution with acetone, added in slight excess of the amount required to produce incipient cloudiness. The mixtures were then warmed until they became homogeneous, and cooled slowly until the phases separated again. The precipitates were reprecipitated several times with acetone from benzene, in order to purify them. It was shown conclusively that degradation did not occur in this procedure. This is a very thorough and important study.

In the same year, Alfrey, Bartovics, and Mark (27) fractionated polystyrene, also for osmotic-pressure and viscosity measurements. A 2 per cent solution in methyl ethyl ketone was titrated with methanol until cloudiness appeared, and warming and slow cooling was used, as by Flory, to ensure equilibrium conditions during precipitation. The fractions were purified by reprecipitation with methanol from toluene solution, and subjected to two consecutive refractionations; the total number of fractions obtained was twenty.

Kunc and Miller (310) in 1941 patented a method of fractionally precipitating isoölefin polymers from solution in hydrocarbon and other non-polar solvents by aliphatic oxygen-containing precipitants; as examples they described the precipitation of polyisobutylene from benzene with acetone, and from carbon disulfide with ethyl ether.

Kemp and Straitiff (144) in 1944 fractionated Buna S by precipitating a 2 per cent benzene solution with methanol. This was done by adding a 1:1 methanol–benzene solution slowly with vigorous stirring until cloudiness appeared, and separating the supernatant liquid from the precipitate by decantation at 20°C. The authors concluded from their results that the distribution of Buna S is too broad, resulting in poor processing characteristics.

(b) Fractional precipitation by cooling

It has been pointed out many times (27, 58, 90, 243, 251) that the precipitation point of a polymer–solvent–precipitant system depends very markedly on the temperature; rather careful control of temperature during a fractional precipitation is therefore necessary, a fact that many authors have failed to realize. This temperature dependence of solubility (and of the partition coefficient of each molecular species of the polymer) can be and has been used in carrying out fractionations; in fact, Mark (176) maintains that a better resolution can be obtained in this way than by the more usual methods just described. The process is somewhat analogous to fractional crystallization in low-molecular chemistry, but the precipitates are not usually crystalline.

In 1929, a process was described (308) by which cellulose acetate could be fractionated by cooling a solution in a mixture of benzene and methanol or ethanol; it was claimed that the higher fractions give filaments, films, lacquers, and other commercially valuable products, with properties superior to those of similar products made from the unfractionated material.

Staudinger and Bondy (271) in 1930 found that balata, a naturally occurring geometrical isomer of rubber, could be fractionated[12] by cooling a warm solution in benzene, toluene, or xylene. In the method described, 17 g. of balata was dissolved in 500 cc. of xylene at 25°C., cooled to 10°C. with constant stirring, and allowed to stand for 24 hr. at that temperature; the mixture was then separated by centrifugation and decantation. This procedure was repeated until the last portion had to be separated by precipitation with a methanol-acetone mixture; this was fraction I. The other fractions were obtained by repeating the procedure on the combined precipitates. Five fractions were prepared in this way.

Scheidegger (311) in 1934 used fractional precipitation by cooling to purify cellulose acetate; benzene-ethanol or benzene-methanol mixtures were the solvents. He claimed that the precipitated fraction decomposed at a higher temperature, and gave less brittle films, than the original material.

By far the most important work[13] in this field has been done on natural rubber by Midgley and his associates (186–193) in the period 1931–42. Their method (186, 187, 189) was based on precipitation from solution by slow cooling. Crepe rubber and benzene were heated together to 50°C., and a solution of (absolute) alcohol and benzene was added slowly, with stirring, until the rubber was completely dissolved. The solution was then cooled slowly to a temperature 1°C. below that at which turbidity is first observed (the precipitation point) and kept at that temperature for 1 hr. The two phases that formed (supernatant and "gel") were separated by decantation. From the supernatant phase a rubber fraction was recovered by chilling in an ice bath; the resulting mother liquor was warmed and the "gel" phase dissolved in it by warming and stirring. These steps were repeated three times, yielding altogether four fractions, A_1, A_2, A_3, and A_4. When an attempt was made to obtain a fifth in the same way, the precipitate did not completely dissolve even at the boiling point of the mixture. From the supernatant liquid a fraction A_5 was obtained, and from the residue (by extraction with benzene in a Soxhlet apparatus) a soluble fraction A_6, and an insoluble fraction B. As the purpose of the process was to effect a purification, and as most of the impurities were in the B and other high fractions, the first three fractions only were refractionated until nitrogen-free rubber was obtained. Later (190) the importance of preventing degradation by oxygen and

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[12] Balata is a high polymer which does precipitate in crystalline form.

[13] A good discussion of this work as a whole may be found in Whitby (23).

light was realized, and the precautions were taken of excluding light and working in a vacuum or in an atmosphere of carbon dioxide. It was found that there was little advantage in refractionating more than twice, as the product of the third fractionation was only slightly better than that of the second. The fractions were characterized by determining the "standard precipitation point", or s.p.p. (190), that is, the temperature at which a sudden increase in turbidity appears in a slowly cooled solution of standard composition. From this study it was concluded that 50 per cent or more of the purified rubber (rubber hydrocarbon) is one soluble component, and that the remainder is composed, in about equal proportions, of an insoluble component and a mixture of other soluble components. This view was in opposition to the "two-phase" theory of rubber, according to which rubber hydrocarbon consists of two components, often called sol and gel. Milled rubber, however, was found (191) to consist of a continuous series of soluble components. In another investigation (192), fractional precipitation was used to determine the molecular weight of rubber, as follows: Rubber was combined with sulfur and separated by fractional precipitation into three fractions, which were analyzed for sulfur; as the sulfur contents were found to be in the ratio of 1:2:3, it was assumed that the fractions were the mono-, di-, and tri-sulfides, and from the amount of sulfur present the molecular weight of rubber was calculated.

Kemp and Peters (141) in 1941 attempted to fractionate rubber by cooling a solution in 68:32 benzene-alcohol to 0°C., but found the results disappointing. Rath and Dolmetsch (223) in 1938 suggested that a solution of cellulose in sodium hydroxide could be precipitated fractionally by cooling, as well as by the addition of a precipitant or of acid; it is known from fractional solution studies that the alkali solubility of cellulose is very sensitive to changes of temperature.

(c) Tabular summary of fractional precipitation methods

In order to facilitate a rapid survey of the methods that have been used, the most important facts relating to each are summarized in table 1.

2. Fractional solution

In a fractional solution procedure, the polymer is placed in contact with a solvent-non-solvent mixture, and the system is allowed to come to equilibrium; after the supernatant solution is decanted, the residue is treated with a fresh mixture, richer in solvent than the first, and this process is repeated until the polymer has all dissolved, or until no more will dissolve. In this way the low-molecular fractions are extracted first, the high-molecular ones last.

In this connection, mention should be made of the so-called "solid-phase rule" (14) ("Bodenkörperregel") studied by Ostwald (208, 209, 210) and Neuenstein (200) and noted by Davidson (60). It is based on the observation that the solubility of a polymer, such as cellulose, differs from ordinary solubility in that the amount dissolved depends on the amount of undissolved solid in contact with the solution. This is most readily explained in terms of heterogeneity of the material; in fact, it is rather good proof of the existence of heterogeneity, if indeed any is needed. For, when a certain amount of polymer is in contact with its solution, the solution may be saturated with respect to the high-molecular-weight constituents, but not with respect to the low ones (14); therefore, if the quantity of the solid phase is increased, more of the low-molecular-weight material will go into solution.

The determination of "alkali solubles" (15, 268) is a standard analytical method in cellulose chemistry; in the usual method, three arbitrarily defined fractions, α-, β-, and γ-cellulose, are separated and weighed; these, of course, differ in their average degree of polymerization, and thus the determination shows a good correlation with the mechanical properties that depend on degree of polymerization. For a more exact characterization, Sakurada (229, 230, 231, 232, 234) recommended the determination of the "solubility curve". Among the cellulose solvents, he studied mainly cuprammonium. Brownset and Davidson (45) investigated the solubility in 2.5 N sodium hydroxide at -5°C., and Brownset and Clibbens (44) the solubility in Triton B (trimethylbenzylammonium hydroxide) and Triton F (dimethylbenzylammonium hydroxide). The solubility curve is obtained by plotting the amount dissolved against the "solvent power" of the solvent, and the shape of the curve is that of the integral distribution curve (S-shaped). Solvent power depends essentially on the composition of the solution used as solvent (e.g., the concentration of a sodium hydroxide solution, or the copper content of a cuprammonium solution); it can, according to Sakurada (234), be determined by comparing solubility curves of the same sample in a series of liquid mixtures, in which one component is the solvent in question, the other a non-polar indifferent liquid. Taniguchi (288) described a method for determining the "normal" solubility curve by making up a homogeneous mixture of polymer, solvent, and non-solvent (where the solvent has a lower boiling point than the non-solvent), and letting it evaporate very slowly at room temperature; under these conditions precipitation takes place so slowly that entanglement and other intermolecular interaction cannot interfere with it.

Like those involving fractional precipitation, fractional solution procedures can be classified according to whether it is the composition of the extracting mixture or the temperature that is being varied. As there are comparatively few examples of the latter process, the two methods will be discussed together.

(a) Methods of fractional solution

(1) Rubber: A very important and very thorough study of the fractional solution of rubber was undertaken by Bloomfield and Farmer (39) in 1940. Extreme precautions were taken to avoid degradation: the work was done in a semi-dark room, in an atmosphere of purified nitrogen, and with added antioxidant (β-phenylnaphthylamine); even the acetone extraction of the rubber and the purification of the solvents were carried out under nitrogen. The rubber was extracted continuously, with mixtures of petroleum ether (solvent) and acetone (non-solvent)—25 per cent petroleum ether for the first fraction, 50 per cent for the second, and other suitable mixtures for higher fractions. Three or four extractions were done with separate samples of each mixture, to ensure complete

TABLE 1

Tabular summary of fractional precipitation methods

POLYMER	SOLVENT	PRECIPITANT	CONCENTRATION OF SOLUTION	NUMBER OF FRACTIONS	YEAR OF PUBLICATION	AUTHOR(S) AND REFERENCES
Rubber	Benzene	Benzene–alcohol (1:1)	3%	2	1924	Pummerer and Koch (218)
Rubber	Benzene, hexahydrotoluene, petroleum ether, or ethyl ether	Alcohol or acetone		2	1927	Pummerer and Miedel (219)
Rubber	Varied	Varied	Varied	8	1928	Pummerer and Miedel (220)
Rubber	Benzene or ethyl ether	Ethanol		6	1939	Kovarskaya and Lipatov (147)
Rubber	Chloroform	Methanol			1941	Kemp and Peters (141)
Hydrorubber	Ethyl ether	Ethanol		5	1930	Staudinger and Schaal (280)
Cellulose nitrate	Acetone	Water or acetone–water	5%	3	1920	Duclaux and Wollman (74)
Cellulose nitrate	Acetone	Benzene			1925	Bréguet (41)
Cellulose nitrate	Acetone	Acetone–water (1:1)		2	1928	Kumichel (153)
Cellulose nitrate	Acetone	Water			1929	Duclaux and Nodzu (73)
Cellulose nitrate	Acetone	Water–acetone (1:4)	16%	4	1930	Beck, Clément, and Rivière (35)
Cellulose nitrate	Acetone–water	Vacuum distillation	5%	11	1930	Beck, Clément, and Rivière (35)
Cellulose nitrate	Acetone	Water			1933	Duclaux and Barbière (72)
Cellulose nitrate	Acetone	Water		9	1933	Medvedev (182); Medvedev and Denisov (183)
Cellulose nitrate	Acetone, ethyl acetate, or benzene	Water			1934, 1935	Glikman (Glückmann) (107–109, 111, 112)
Cellulose nitrate	Acetone–water	Vacuum or ordinary distillation			1935	Glikman (111)
Cellulose nitrate	Acetone	Water		3	1935	Rogovin and Glazman (225)
Cellulose nitrate	Acetone	Water			1936	Schulz (243)
Cellulose nitrate	Acetone	Heptane		17	1938	Spurlin (264)
Cellulose nitrate	Acetone	Water or ethanol			1938	Rath and Dolmetsch (223)
Cellulose nitrate	Acetone	Water		4–7	1939	Staudinger and Jurisch (278)
Cellulose nitrate	Acetone	Water	0.5%		1940	Jurisch (138)
Cellulose nitrate					1941–1942	Schulz *et al.* (252, 254)
Cellulose acetate	Acetone	Water			1923	Mardles (172)

Cellulose acetate	Acetone	Acetone–water (1:1)	3%		1928	Caille (46)
Cellulose acetate	Acetone	Water–acetone (3:1)	10%		1929	McNally and Godbout (171)
Cellulose acetate	Acetone	Water		3	1930	Rocha (224)
Cellulose acetate	Acetone	Water		3	1930, 1932	Ohl (205, 206)
Cellulose acetate	Acetone	Water			1931	Iwasaki (130)
Cellulose acetate	Acetone	Water			1931	Caille (47)
Cellulose acetate	Methyl glycol or acetone	Water or petroleum ether			1932	Herzog and Deripasko (119)
Cellulose acetate	Acetone	Water			1934	Clément and Rivière (53)
Cellulose acetate	Acetone	Water			1934	Obogi and Broda (203)
Cellulose acetate	Acetone	Water			1934	Herz (117)
Cellulose acetate	Chloroform	Methanol			1934	Elöd and Schmid-Bielenberg (77)
Cellulose acetate	Chloroform	Methanol			1934	Hess and Ulmann (120)
Cellulose acetate	Acetone	Water	2.5%		1935	Ulmann (293)
Cellulose acetate	Acetic acid–acetone (1:1)	Water		4	1937, 1939	Lachs *et al.* (155–159)
Cellulose acetate	Chloroform	Methanol			1937, 1939	Lachs *et al.* (155–159)
Cellulose acetate	Acetone	Benzene			1938	Levi, Villotta, and Monticelli (164)
Cellulose acetate	Acetone	Ethyl ether			1939	Danilov, Gol'dfarb, and Zaitseva (59)
Cellulose acetate	Acetic acid	Water			1939	Bezzi and Croatta (37)
Cellulose acetate	Acetone	Water			1940	Mark and Simha (180)
Cellulose acetate	Acetone	Ethanol	2.5%	15	1942	Sookne, Rutherford, Mark, and Harris (263)
Ethyl cellulose	Glacial acetic acid	Water			1933	Okamura (207)
Benzyl cellulose	Alcohol–benzene	Alcohol			1936, 1937	Glikman (Glückmann) (110, 113)
Methyl cellulose	Water	Sodium sulfate	2.5%	4	1938	Signer and Liechti (259)
Ethyl cellulose	Dioxane	Water		3	1938	Staudinger and Reinecke (279)
Ethyl cellulose	Alcohol	Gasoline	4%		1939	Ushakov *et al.* (294)
Cellulose xanthogenate	Aqueous pyridine	Methanol or ether	Very dilute		1934	Fink, Stahn, and Matthes (85)
Cellulose	Sodium hydroxide	Sodium sulfate	0.1%		1939	Tydén (291)
Cellulose	0.5 *M* cupriethylenediamine	8 *N* sulfuric acid	1%	8	1942	Strauss and Levy (284)
Cellulose	Sodium hydroxide	Water–acetone			1943	Coppick, Battista, and Lytton (55)

TABLE 1—*Continued*

POLYMER	SOLVENT	PRECIPITANT	CONCENTRATION OF SOLUTION	NUMBER OF FRACTIONS	YEAR OF PUBLICATION	AUTHOR(S) AND REFERENCES
Gelatin	Water	Alcohol		2	1926	Northrop and Kunitz (202)
Gelatin	Water	Ammonium sulfate		2	1927	Nagorny (199)
Glycogen	Formamide	Methanol			1937	Staudinger and Husemann (277)
Glycogen (degraded)	0.1 *N* calcium chloride	Methanol		3	1941	Husemann (129)
Dextrin	Water	Methanol			1942	Levine, Foster, and Hixon (165)
Nitrated wood	Acetone	Alcohol–water		8	1943	Coppick and Jahn (56)
Polyvinyl acetate	Benzene	Petroleum ether	40%	3	1927	Staudinger *et al.* (275)
Polystyrene (hemicolloidal)	Acetone	Acetone	37%	5	1929	Staudinger *et al.* (273)
Polyethylene oxide	Benzene	Ethyl ether		3	1929	Staudinger and Schweitzer (281)
Polyindene	Benzene	Ethanol		7	1928	Whitby and Katz (300)
Polycinnamalfluorene	Benzene	Ethanol		5	1928	Whitby and Katz (300)
Polycinnamalindene	Benzene	Ethanol		4	1928	Whitby and Katz (300)
Polystyrene	Benzene	Ethanol	1.5%	3	1930	Whitby (297)
Polyindene	Chloroform	Ethanol	40%	3	1930	Whitby and Katz (299)
Polystyrene	Benzene	Ethanol		6	1932	Whitby (298)
Polystyrene	Benzene	Acetone		4	1932	Staudinger (21)
Polystyrene	Benzene	Methanol–acetone			1934	Daneš (58)
Polystyrene	Methyl ethyl ketone	Methanol		7	1936	Schulz and Husemann (251)
Polystyrene	Chloroform, benzene, tetralin, carbon disulfide, dioxane, or pyridine	Methanol			1936	Dobry and Schwob (67)
Sodium butadiene polymer	Benzene	Methanol, ethanol, propanol, phenol, or acetone	Varied		1936	Komarov and Selivanova (146)
Vinyl ester	Acetone	Acetone–water			1936	Douglas and Stoops (71)
Sodium bivinyl polymer	Benzene	Ethanol	1%	4	1938	Zhukov and Komarov (305)
Polymethyl methacrylate	Benzene	Cyclohexane			1941	Schulz and Dinglinger (250)
Polyvinyl acetate	Acetone	Methanol–water (1:1)			1941	Blease and Tuckett (38)

Polyvinyl chloride.........	Mesityl oxide or cyclohexanone	Methanol (acetone as diluent)	0.5–1%		1941	Fuoss (95)
Polyisobutylene............	Benzene	Acetone	5%	5	1941	Kunc and Miller (310)
Polyisobutylene............	Carbon disulfide	Ethyl ether	10%	8	1941	Kunc and Miller (310)
Polyisobutylene............	Benzene or toluene	Acetone or methanol			1942	Staudinger *et al.* (270)
Polymethacrylonitrile......	Acetone	Methanol	1%		1942	Kern and Fernow (145)
Polyvinyl chloride.........	Acetone	Methanol			1943	Fuoss and Mead (96)
Polyisobutylene............	Benzene	Acetone	1%		1943	Flory (90)
Polystyrene................	Methyl ethyl ketone	Methanol	2%	20	1943	Alfrey, Bartovics, and Mark (27)
Buna S.....................	Benzene	Methanol	2%	2	1944	Kemp and Straitiff (144)
Cellulose acetate..........	Benzene–methanol or benzene–ethanol	Cooling	10%		1929	British Celanese Ltd. (308)
Balata.....................	Benzene, toluene, or xylene	Cooling	3–4%	5	1930	Staudinger and Bondy (271)
Cellulose acetate..........	Benzene–ethanol or benzene–methanol	Cooling	5–15%	2	1934	Scheidegger (311)
Rubber.....................	Alcohol–benzene	Cooling		7	1931–1942	Midgley *et al.* (186–193)
Rubber.....................	Alcohol–benzene	Cooling	3%	Unsuccessful	1941	Kemp and Peters (141)
Cellulose..................	Sodium hydroxide	Cooling			1938	Rath and Dolmetsch (223)

extraction of that fraction. The extractions were carried out under static conditions, except for slow rotation on rollers about a horizontal axis for 2-hr. periods. The fractions were isolated by evaporation under reduced pressure in a current of nitrogen. Four fractions were obtained. Their physical properties were measured by Gee and Treloar (103), and relationships between molecular weight and physical properties established.

A similar method was used by Kemp and Peters (141) in 1941, with acetone–hexane mixtures as solvents for the extraction. Light was excluded, and the work was done under nitrogen.

(2) Cellulose and its derivatives: Uchida (292) in 1930 determined the solubilities of nitrocellulose in a variety of ethyl ether–ethanol mixtures at various temperatures, and characterized the soluble and insoluble fractions by their nitrogen contents.

The first thorough study in the field is due to Craik and Miles (57), who in 1931 fractionally extracted nitrocellulose with acetone-water solutions at controlled temperatures. The advantage claimed for this method as compared with Duclaux's precipitation method is that any number of fractions can easily be obtained. Two variations of the method were used: one in which the residue insoluble in one solution was subsequently treated with one richer in solvent; and another "analytical" one, in which a fresh sample was used every time, and treated with the various solutions. The viscosities of the fractions were found to differ.

In 1933, Berl and Hefter (36) fractionated nitrocellulose by extraction with ethyl ether–ethanol solutions; the nitrogen contents of the fractions usually differed. In the same year, Yamamoto (304) fractionally extracted nitrocellulose with acetone–water solutions; in this case also, separation according to the degree of nitration resulted.

In 1934, Clément and Rivière (53) studied the fractional solution of cellulose acetate, using aqueous methanol or aqueous ethanol. Again, the fractions differed chemically as well as in physical properties. In the same year, Taniguchi and Sakurada (289) applied a similar procedure to cellulose dextrin acetate, and to triacetylcellulose. Acetone-benzene solutions were used in each case; the cellulose dextrin acetate yielded five fractions, the triacetylcellulose four.

In 1934 also, Correns (309) invented a process in which cellulose acetate was fractionally dissolved in various mixtures of acetone and ethanol; the insoluble fraction showed superior properties for the production of films and filaments, while the soluble part was suitable for lacquers.

In the same year, Fink, Stahn, and Matthes (85) effected a fractionation of cellulose xanthogenate (viscose) by extraction with aqueous pyridine or dioxane. The two fractions obtained differed both in chain length and in chemical composition.

Davidson in 1934 (60) and 1936 (61) studied the solution of modified cellulose (oxy- and hydro-celluloses) in the hydroxides of sodium, lithium, potassium, and tetramethylammonium. A fractional extraction of hydrocellulose with sodium hydroxide was effected by varying the concentration (from 2.25 N to

2.5 *N*) and the temperature (from 0°C. to -5°C.). The dissolving power of lithium hydroxide and tetramethylammonium hydroxide proved to be similar, but that of potassium hydroxide was less, and not as much affected by temperature.

Abel and Hess (24) in 1935 observed that the extract of trimethylcellulose with hot benzene yields, on cooling, one fraction that is soluble in cold benzene, and another that is insoluble. By repeating the procedure, a reversibly soluble fraction was finally obtained. These effects, which the authors call "false solubility", are readily explained on the basis of heterogeneity—the reversibly soluble fraction has become reasonably homogeneous because of repeated fractionation. The action of other solvents was described.

In 1935, Staud and Yackel (312) described a process for fractionating cellulose acetate on a commercial scale by stirring it with a solvent mixture consisting of acetone and water, or acetic acid and water. They claimed that the residue (which showed a higher viscosity than the soluble fraction, but the same acetyl content) gave more flexible and more water-resistant films than the original material.

Mark and Saito (179) in 1936, in reviewing various possible fractionation procedures for cellulose acetate, mentioned fractional solution with benzene–methyl acetate mixtures. The fractions were said to differ in viscosity, but not in acetyl content. In the same year Rogovin and Glazman (226) fractionated cellulose acetate by solution in acetone–water mixtures and found that separation with respect to chemical nature could be effected. Neumann, Obogi, and Rogovin (201) in 1936 treated cellulose from three sources (cotton linters, sulfite pulp, and viscose rayon) by two fractional solution methods: (*1*) using sodium hydroxide of fixed concentration and changing the temperature; (*2*) using cuprammonium solution of varying copper content. In (*1*), the sodium hydroxide concentration was 12 per cent, the time of extraction 30 min., and the temperature 15°C., 0°C., -5°C., and -12°C.

O'Dwyer (204) in 1937 separated oak hemicellulose into two fractions by digesting the sample with the enzyme takadiastase and extracting with water, or, as in one case, by extracting with water without the prior use of an enzyme.

Kumichel (154) in 1938 described the fractional solution of cellulose in cuprammonium solutions of gradually increasing copper content. Rath and Dolmetsch (223) in 1938 used fractional solution of nitrocellulose in acetone-water solutions. Dolmetsch and Reinecke (68, 69) in 1939 extracted cellulose with 10 per cent sodium hydroxide (making temperature the variable), and nitrocellulose with various mixtures of acetic acid and ethanol, or acetone and ethanol. In 1939, Schieber (238, 239, 240, 241) discussed the fractionation of cellulose, and came to the conclusion that fractional solution in sodium hydroxide is unsatisfactory, because the solubility of the high fractions is too low and there is a danger of degradation. He nitrated the cellulose carefully, using a mixture of phosphoric acid and fuming nitric acid at 18°C., and fractionated the nitrate by solution in ethanol–ethyl acetate or ethanol–acetic acid mixtures. Böhringer and Seyfert (40) in 1939 studied the changes in molecular-weight distribution that take place on washing and bleaching textiles, by means of fractional solution of the nitrate. Eisenhut (75) in the same year recommended fractional washing with sodium hydroxide, as a method for characterizing staple fiber. Morozov (196), in 1939, fractionated cotton cellulose with a mixture containing 1.35 per cent copper, 15.5 per cent ammonia, and 0.02 per cent sucrose, and other mixtures prepared from the first one by stepwise dilution with water.

Staudinger and Eder (274) in 1941 fractionated highly degraded cellulose triacetate by solution in chloroform.

In 1942, Ekenstam (76) used phosphoric acid of varying concentration in the range of 73–83 per cent for the fractional solution of the cellulose in rayon pulp and in finished rayon.

In 1943, Atchison (27a) described in some detail the fractionation of several cellulose nitrates. As extracting media, he used solutions of ethyl acetate and absolute ethyl alcohol.

(*3*) *Other natural products:* In 1935, Liepatoff and Putilowa (166) applied the method to gelatin, using water at various temperatures, and obtained four fractions. Lampitt, Fuller, and Goldenberg (161) in 1941 treated starch in a similar way and obtained a water-insoluble fraction (α-amylose), a fraction soluble in hot water (β-amylose), and one soluble in cold water ("soluble starch").[13a]

(*4*) *Synthetic products:* Staudinger, Frey, and Starck (275) reported two methods for fractionating polyvinyl acetate in 1927: the first, by precipitation, has already been described; in the second one fraction was obtained by extracting with butanol, another by dissolving the residue in benzene and precipitating with butanol, and a third from the resulting supernatant liquid. Staudinger (20) described a fractional solution method for hemicolloidal polystyrenes, in which, instead of using binary mixtures of varying composition, he used different single solvents in succession for the extraction. Methanol was used to dissolve out the lowest members (degree of polymerization 1–10), hot butanol the next fraction (10–30), and acetone the higher members (30–60); fractional precipitation with acetone or methanol was used for the highest members.

In 1936, Douglas and Stoops (71) reported an analytical precipitation procedure for vinyl esters; this has been described above. In order to determine the width of the bands in this procedure, they fractionated two of the resins completely by a fractional extraction process, obtaining twenty-five fractions from each. A similar purpose was served by the fractionation of coumarone–indene varnish resin reported by Adams and Powers (25) in 1943; these authors wished to correlate their precipitation titration studies with an actual distribution curve, and for that purpose fractionated the above-mentioned resin by fractional solution, obtaining seven fractions.

Rogovin and Tsaplina (227) in 1941 demonstrated the polydispersity of

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[13a] A recent review, by T. J. Schoch, of methods in use for the separation of starch into the usual two fractions may be found in *Advances in Carbohydrate Chemistry*, Vol. I, W. W. Pigman and W. L. Wolfrom (*Editors*), pp. 247–77. Academic Press, Inc., New York (1945).

samples of polyvinyl chloride by fractional solution in acetone at room temperature and at 40–45°C.

Sebrell (256) in 1943, in the course of a comparison of the properties of natural rubber with those of several synthetic rubbers, carried out a fractionation of Buna S by extraction with petroleum ether-benzene solutions, and alcohol-petroleum ether solutions for the lowest members. It was found that fractionation is less efficient in the high than in the low molecular-weight range. A more rapid (analytical) method was also tried, in which separate portions of the original sample were extracted with the various mixtures.

Kemp and Straitiff (144) in 1944 described a method for extracting the low polymer from Buna S by using methanol–benzene solutions, of a concentration in the neighborhood of 20 per cent by volume of methanol. The extracted fraction constituted 42 per cent of the original by weight.

(b) Tabular summary of fractional solution methods

The methods described above are summarized, for more convenient reference, in table 2.

3. Comparison of fractional precipitation and fractional solution methods

There have been many objections raised against fractional precipitation methods. Craik and Miles (57) criticized Duclaux's (74) method on the grounds that (*1*) 5 per cent of the original material is lost in the precipitations, (*2*) when water is added drop by drop, three layers are sometimes formed, which can be separated only with difficulty, (*3*) there is little choice as to the size and number of fractions, for the first one is always large (50–75 per cent of the total). They claimed that with solution methods any number and size of fractions can be obtained, and that there are no losses in the process. Rogovin and Glazman (226) also pointed out the disadvantages of Rocha's (224) method, claiming (*1*) that overlapping of fractions occurs because the longer molecules pull the shorter ones down into the precipitate while the shorter keep the longer ones in solution, by entanglement and other forms of interaction, (*2*) that the reproducibility of the results is not good, (*3*) that a limited number of fractions only can be obtained in one run, so that refractionation is necessary, and (*4*) that fractionation is effected only with respect to molecular size, not with respect to the degree of chemical substitution. Dolmetsch and Reinecke (68) claimed that precipitation methods suffer from (*1*) an overlapping of fractions as a result of entanglements, (*2*) lack of reproducibility, and (*3*) the difficulty of making a clean separation of the two phases. Sakurada and Taniguchi (235) also drew attention to several disadvantages of the method: (*1*) the initial complete solution that is necessary can often be effected only by means that cause partial breakdown; (*2*) results are difficult to reproduce for, since equilibrium is attained so slowly, the amount of precipitate depends on the length of the interval between the addition of precipitant and separation; and (*3*) a substance that, when added in certain proportions, can decrease the dissolving power of a solvent—and thereby act as a precipitant—may in other proportions actually increase it. Bloomfield and Farmer (39) adopted the fractional solution procedure (at Gee's suggestion)

TABLE 2

Tabular summary of fractional solution methods

POLYMER	EXTRACTING MIXTURE	VARIABLE	NUMBER OF FRACTIONS	YEAR OF PUBLICATION	AUTHOR(S) AND REFERENCES
Rubber	Petroleum ether–acetone	Composition	4	1940	Bloomfield and Farmer (39)
Rubber	Hexane–acetone	Composition		1941	Kemp and Peters (141)
Cellulose nitrate	Ethyl ether–ethanol	Composition or temperature	2	1930	Uchida (292)
Cellulose nitrate	Acetone–water	Composition		1931	Craik and Miles (57)
Cellulose nitrate	Ethyl ether–ethanol	Composition		1933	Berl and Hefter (36)
Cellulose nitrate	Acetone–water	Composition		1933	Yamamoto (304)
Cellulose acetate	Water–methanol (or ethanol)	Composition		1934	Clément and Rivière (53)
Cellulose acetate	Acetone–ethanol	Composition	2	1934	Correns (309)
Cellulose dextrin acetate	Acetone–benzene	Composition	5	1934	Taniguchi and Sakurada (289)
Cellulose triacetate	Acetone–benzene	Composition	4	1934	Taniguchi and Sakurada (289)
Cellulose xanthogenate	Pyridine–water or dioxane–water		2	1934	Fink, Stahn, and Matthes (85)
Oxycellulose or hydrocellulose	Hydroxides of sodium, lithium, potassium, or tetramethylammonium	Composition or temperature		1934, 1936	Davidson (60, 61)
Trimethylcellulose	Benzene	Temperature		1935	Abel and Hess (24)
Cellulose acetate	Acetone–water or acetic acid–water		2	1935	Staud and Yackel (312)
Cellulose acetate	Benzene–methyl acetate	Composition		1936	Mark and Saito (179)
Cellulose acetate	Acetone–water	Composition		1936	Rogovin and Glazman (226)
Cellulose	Sodium hydroxide (12%)	Temperature		1936	Neumann, Obogi, and Rogovin (201)
Cellulose	Cuprammonium	Copper content		1936	Neumann, Obogi, and Rogovin (201)
Oak hemicellulose	Enzyme digestion and water		2	1937	O'Dwyer (204)
Cellulose	Cuprammonium	Copper content		1938	Kumichel (154)
Cellulose nitrate	Acetone–water	Composition		1938	Rath and Dolmetsch (223)
Cellulose	Sodium hydroxide (10%)	Temperature		1939	Dolmetsch and Reinecke (68, 69)
Cellulose nitrate	Acetic acid–ethanol or acetone–ethanol	Composition		1939	Dolmetsch and Reinecke (68, 69)
Cellulose	Sodium hydroxide	Temperature		1939	Schieber (238–241)

Cellulose nitrate...............	Ethanol–ethyl acetate or ethanol–acetic acid	Composition		1939	Schieber (238–241)
Cellulose nitrate...............	?			1939	Böhringer and Seyfert (40)
Cellulose......................	Sodium hydroxide	?		1939	Eisenhut (75)
Cellulose......................	Cuprammonium	Concentration		1939	Morozov (196)
Degraded cellulose triacetate..	Chloroform			1941	Staudinger and Eder (274)
Cellulose......................	Phosphoric acid (73–83%)	Concentration		1942	Ekenstam (76)
Cellulose nitrate...............	Ethanol–ethyl acetate	Composition		1943	Atchison (27a)
Gelatin........................	Water	Temperature	4	1935	Liepatoff and Putilowa (166)
Starch.........................	Water	Temperature	3	1941	Lampitt, Fuller, and Goldenberg (161)
Polyvinyl acetate..............	Butanol–benzene	Composition		1927	Staudinger, Frey, and Starck (275)
Hemicolloidal polystyrene.....	Methanol–butanol–acetone	Nature of solvent		1932	Staudinger (20)
Polyvinyl esters..............	?		25	1936	Douglas and Stoops (71)
Polyvinyl chloride.............	Acetone	Temperature		1941	Rogovin and Tsaplina (227)
Coumarone–indene resin.......	?		7	1943	Adams and Powers (25)
Buna S........................	Petroleum ether–benzene or alcohol–petroleum ether	Composition		1943	Sebrell (256)
Buna S.......................	Methanol–benzene		2	1944	Kemp and Straitiff (144)

mainly because of the danger of entangled clusters of molecules precipitating "en bloc" in a fractional precipitation method.

Most of the objections to fractional precipitation disappear when the solution is made sufficiently dilute. Precipitation "en bloc" occurs only when the solution is concentrated enough to allow interaction between the molecules; moreover, there is no reason why chain entanglements in the solid sample should not cause a similar difficulty in the solution process. It is true, of course, that solution occurs much more slowly than precipitation, as ordinarily carried out, and hence equilibrium conditions are more likely to be maintained. However, precipitation by cooling can be made to occur as slowly as desired; and even if precipitation be carried out by the addition of precipitant, the technique of heating the mixture above the critical temperature and allowing the final precipitation to occur by slow cooling can always be used. Moreover, if the solution is dilute enough, a greater number of small fractions can be obtained than in a more concentrated one, as may be seen by a consideration of the phase diagram. Diluting the precipitant with the solvent, or with a third liquid, improves the control of precipitation conditions, as does working at a higher temperature, where the solubility is greater. As for the necessity for refractionation, such treatment is desirable (99) in any case, if uniform fractions are to be obtained. Indeed, Spurlin (264) rejected fractional solution in favor of precipitation because the former method does not so readily permit refractionation.

Mark (176) suggested that it would be profitable to compare results obtained by the two methods when used on the same material. He found that, in the case of cellulose nitrate precipitated with heptane from butyl acetate or acetone solution and extracted with alcohol–ethyl acetate mixtures of varying compositions at constant temperature, the results of the two methods were in good agreement.

Kemp and Peters (141) made a comparison of several procedures as applied to rubber: fractional diffusion into a single solvent (to be discussed in the next section), fractional solution by a method similar to that of Bloomfield and Farmer, combined diffusion and precipitation, and fractional cooling; they decided in favor of the combined diffusion and precipitation process.

Jurisch (138) prefers precipitation to solution methods. He considers the latter to have the following disadvantages: (*1*) there is considerable overlapping of the molecular-weight ranges of the fractions (as he showed by comparison with fractional precipitation results obtained for the same sample); (*2*) the swelling of the undissolved residue is so great that the solvent power of extracting mixtures cannot be increased beyond a certain value, without making the phases very difficult to separate; (*3*) insoluble impurities accumulate in the residue, whereas in fractional precipitation they can be removed by filtering before the precipitant is added.

For the fractionation of cellulose, however, solution methods are usually preferable to precipitation. As Neumann, Obogi, and Rogovin (201) pointed out, it is extremely difficult to effect complete solution of a cellulose sample in any solvent, without risking the danger of breakdown by the drastic treatment necessary. In spite of this difficulty, however, Coppick, Battista, and Lytton (55) succeeded in dissolving cellulose completely in sodium hydroxide, and were thus able to fractionate it by precipitation. Another solvent, in which complete solution is claimed to take place easily without degradation, is cupriethylenediamine, as suggested by Strauss and Levy (284).

Some polymers are heterogeneous in more than one respect. The molecules of cellulose nitrate, for example, differ both in chain length and in degree of nitration. In such instances it may be desirable sometimes to prepare fractions of relatively uniform chain length, at other times fractions of relatively uniform composition. No method has been reported that effects a separation solely on the basis of composition, but many methods yield fractions that differ from each other in both respects. (For examples, see previous sections and references 36 and 179.) If from a fractionation study conclusions are to be drawn as to relationships between chain length and physical properties, it should always be definitely established that the fractions are identical in chemical composition.[14]

4. Distribution between two immiscible solvents

In precipitation and solution methods, the solvent and non-solvent are completely miscible; only the presence of polymer (in amounts above the critical value) causes a separation into two phases. It is also possible, however, to use a solvent system which is heterogeneous even in the absence of polymer; as Brønsted (42) and Schulz and Nordt (255) have shown, the distribution of polymer molecules in such a system depends on molecular weight. A fractionation can, therefore, be accomplished by varying the composition of one of the phases.

Such a method was applied in 1940 by Schulz and Nordt (255) to polyethylene oxide (which they found could not be fractionated by precipitation, because the crystalline nature of the precipitate made it difficult to maintain equilibrium). In the solvent system one phase was water, and the other a solution of chloroform and benzene; the percentage of benzene was decreased stepwise in the separation of successive fractions. The volume of the water layer was kept large compared to that of the other, for theoretical considerations showed that this improved the efficiency of separation. In order to ensure equilibrium and yet prevent emulsification, the two phases were stirred separately and in opposite directions.

A similar method was applied in 1941 by Lovell and Hibbert (169) to lignin. They used the solvent system methanol–water–chloroform–carbon tetrachloride, effecting separation by varying the concentration of the chloroform. Fractions differed both in viscosity and in methoxyl content.

Although this method has as yet been applied only in these two instances, it could be used with any high polymer, provided that a suitable solvent system could be found. Schulz and Nordt (255), however, express the opinion that

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[14] It is important to note that such considerations apply especially to synthetic copolymers, for in such substances compositional heterogeneity is the rule. For example, Buna S molecules of the same weight may differ widely in styrene content.

fractional precipitation is more efficient and should be used in preference whenever applicable.

B. RATE-OF-SOLUTION (DIFFUSION) METHODS

Although the methods to be described in this section are sometimes classed with fractional solution methods, they should be treated separately, as they are based on a different principle. The separation according to molecular size does not, as in the previous section, depend on the difference in the solubility of the larger and the smaller molecules, but on the difference in their rate of solution or diffusion. Whereas in solubility methods equilibrium conditions prevail (or should prevail), in diffusion methods fractions are separated as they are still diffusing, before equilibrium is established. The method involves placing the polymer in contact with a solvent, removing the supernatant solution after a definite time interval, replacing it with fresh solvent, and repeating the procedure until the desired number of fractions has been obtained. As would be expected, the smaller molecules concentrate in the first fractions and the larger ones in the last, for the smaller molecules diffuse more rapidly and are, therefore, first extracted.

Although fractional solution and diffusion differ in principle, it is often difficult to classify a particular method, because of an uncertainty as to whether or not equilibrium conditions existed. In this review we have classified as diffusion methods those in which a single solvent is used, at a single temperature, in successive extractions; and as fractional solution methods those in which either the composition of a mixed solvent, or the temperature at which it is used, is varied in successive extractions. It is freely admitted that this classification is somewhat arbitrary, as it is possible to separate two fractions (but not more than two) by extraction with a single solvent at a single temperature, when equilibrium conditions are maintained.

(a) Applications of the diffusion methods

(*1*) *Rubber:* Most of the diffusion experiments have been done with natural rubber, and are closely associated with early theories about the "two-phase" nature of rubber.

As early as 1887, Engler and Herbst (79) knew that rubber is only partly soluble in solvents such as ether, chloroform, benzine, benzene, and carbon disulfide; they described the properties of the two fractions obtainable, and concluded that "in rubber two isomers are combined". Gladstone and Hibbert in 1888 (106) confirmed these observations. Weber (295, 296) in 1900 described an extraction with chloroform, and concluded that the fractions are not chemically identical, as the insoluble part contained combined oxygen. In 1912, Beadle and Stevens (34) used benzene for the separation, and likewise emphasized the lack of purity of the insoluble fraction, focusing attention, however, on the nitrogen rather than the oxygen content. Caspari (51) in 1913 recommended petroleum ether as the solvent, because it gives a more complete separation and produces less swelling of the insoluble part, thus giving a more distinct boundary between the phases. The terms "soluble" and "pectous" (insoluble) rubber were applied to the two fractions. Two extraction methods were described: one continuous, by which quantitative separation was claimed to have been effected after 10 hr.; the other, static. These experiments were criticized in 1919 by Stevens (282), who pointed out that the amount dissolved depends on many variables besides the nature and source of the rubber,—namely, the nature of the solvent, the time of extraction, the temperature, and the age of the specimen. In 1925 Feuchter (84) used ethyl ether and petroleum ether as the solvent; he called the two fractions diffusion (or D) rubber, and gel skeleton.

TABLE 3

Tabular summary of diffusion methods

POLYMER	SOLVENT	AUTHOR(S) AND REFERENCES
Rubber	Petroleum ether	Caspari (51), Feuchter (84), Kemp and Peters (139), Gee (97)
	Ethyl ether	Engler and Herbst (79), Feuchter (84), Pummerer *et al.* (214–217, 220, 222), Smith *et al.* (260–262), Midgley and Henne (188)
	Chloroform	Engler and Herbst (79), Weber (295, 296)
	Benzene	Engler and Herbst (79), Beadle and Stevens (34)
	Carbon disulfide	Engler and Herbst (79)
	Hexane	Kemp and Peters (139, 141)
Nitrocellulose in acetone solution	Acetone	Krüger (152)
Nitrocellulose	Ethanol	Duclaux and Nodzu (73)
Polyanethole	Ethyl ether	Staudinger *et al.* (272)
Polyindene	Ethyl ether or petroleum ether	Staudinger *et al.* (269)
Polyvinyl acetate	Acetone	Whitby, McNally, and Gallay (301)
Polystyrene	Ethyl ether, acetone, or diethyl oxalate	Whitby (297)
Sodium bivinyl polymer	Petroleum ether, benzene, or chloroform	Zhukov *et al.* (306)

In the same year, the two-phase theory received further support from a study of the structure of latex particles, by Freundlich and Hauser (93); they found, by using a micromanipulator, that Hevea latex particles consist of a fluid interior (identified with the soluble fraction) surrounded by a solid shell (the gel skeleton) (see also Hauser (3)).

The work of Pummerer (214, 215, 216, 217, 220, 222), on the other hand, threw doubt on the theory. In 1926 he observed (214) that, although the rate of solution of rubber becomes very slow after about 3 days in contact with ethyl ether, diffusion does not entirely stop; and also, that milling increases the proportion of the soluble component. It was in this paper that the terms "sol" and "gel" rubber were introduced. In 1928, Pummerer *et al.* (217) described a continuous extraction apparatus for the fractionation of rubber; a fraction was defined as the portion of rubber extracted in 24 hr. In another paper, Pummerer and Miedel (220) compared the extraction process with other purification methods (including fractional precipitation) with respect to the efficiency of purification. Later Pummerer and Pahl (222) described a static extraction with ethyl ether, in which six successive samples of ether were allowed to remain for 3 days in contact with the rubber sample (air and light carefully excluded) and then poured off.

In 1928, Bary and Hauser (32, 33) recommended the terms α- and β-rubber instead of sol and gel. They contended that the possibility of a reversible transformation of α- into β-rubber shows that they form a one-phase system (a jelly), not a two-phase system (a gel); that there may be two components, but not two phases, in the rubber hydrocarbon. An attempt was made to explain the elastic properties of rubber on this basis.

Whitby (297) in 1930 definitely proved that diffusion of rubber into organic solvents never comes to an abrupt end, but rather slows down gradually; he found that after four years one sample was completely dissolved, except for the protein. Even if the point where diffusion becomes very slow is taken as the "end point", the sol-gel ratio still depends on the nature of the solvent. He therefore concluded that instead of a pair there is a continuous series of components, as in synthetic polymers such as polystyrene or polyvinyl acetate. He reaffirmed this in 1932 (298).

In 1933 and 1934, Smith *et al.* (260, 261, 262) prepared pure rubber hydrocarbon, crystallized it, and then separated it into sol and gel by extraction with ethyl ether; they also succeeded in crystallizing the sol and gel fractions, and examined their properties.

Staudinger (22) fractionated rubber by diffusion, and found that the molecular weights of the four fractions differed only slightly.

Midgley and his collaborators (187, 188) again pointed out the fallacy of the two-phase theory. The early workers took it for granted that sol and gel could be separated by extraction with ether, just as sugar and sand would be separated by extraction with water; actually, however, sol and gel are mutually soluble. On the addition of ether, two phases are formed, but these do not correspond to sol and gel; the solution phase consists of the sol fraction and ether, while the insoluble phase contains some sol in addition to gel and ether. There is, therefore, no absolute method for determining sol-gel ratios.

More recently, Kemp and Peters (139) have studied the fractional diffusion process, as applied to rubber. In 1939 they described the method and the apparatus. The solvent was petroleum ether or hexane, the extraction period 72 hr., and the work was carried out under an atmosphere of nitrogen and at a constant temperature. (Petroleum ether was found superior to ethyl ether, as the latter is apt to contain peroxides and therefore cause oxidative breakdown; hexane is even better than petroleum ether. Hexane is also preferable to benzene or tetralin.) In 1941 (141), the same method (with hexane as solvent) was compared with other fractionation procedures; twelve fractions were then obtained. In a combined diffusion and precipitation method, already described, chloroform was used as the solvent.

Gee (97) in 1940 used petroleum ether in the preparation of sol rubber for osmotic-pressure determinations.

The modern ideas about the structure of the rubber hydrocarbon, as far as the sol and gel components are concerned, can be summarized as follows: (*1*) there is no single sol component, but a continuous series of components, differing in the degree of polymerization only, and thus constituting a homologous polymeric series; (*2*) the gel component differs from the sol components in that it is cross-linked (13);[15] (*3*) the sol and gel form a one-phase system; (*4*) the sol-gel ratio can be changed by various treatments, e.g., milling (and therefore reversible sol-gel transformations are possible); (*5*) it is not definitely known what the native state of rubber is, before any treatment is applied. Staudinger (19) suggested that rubber and cellulose may be monodispersed in the native state, and be broken down and made heterogeneous by purification and other treatments. Treatment could cause both depolymerization of the chains, or their cross-linking (e.g., by the action of oxygen or light).

An interesting comparison between an extraction and a precipitation method of fractionation was made by Midgley and Henne (188). They found that sol rubber prepared by a single diffusion into ethyl ether can be separated into two fractions by precipitation from benzene-alcohol by cooling, but the sol prepared by precipitation diffuses completely in ether; this proves the superiority of the precipitation method. Gee (99), in discussing various fractionation procedures, expressed doubt as to whether fractional extraction by a single solvent can ever be made quantitatively reproducible.

(*2*) *Cellulose and its derivatives:* Applications of the fractional diffusion method to cellulose and its esters and ethers are rare.

Krüger (152) in 1928 used a method in which diffusion took place not from the solid phase, but from a solution; he let 20 cc. of a solution of nitrocellulose in acetone, methanol, amyl acetate, and other solvents diffuse against 60 cc. of the pure solvent; after a definite time, four layers could be separated, which differed both in molecular weight and in degree of nitration. Duclaux and Nodzu (73) in 1929 mentioned that nitrocellulose can be fractionated by solution in ethanol.

McNally and Godbout (171) in 1929 used a method which bears the same relationship to diffusion into a single solvent as fractional precipitation does to fractional solution; it, too, depends on the rate of a process rather than on the equilibrium state, but it involves precipitation rather than solution. They

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[15] It might be better to say that the essential difference between sol and gel is one of molecular size. In the preparation of most synthetic polymers branching and cross-linking are probably occurring at all stages of the polymerization. The resulting molecules belong to the gel component when they have reached such a size that they are insoluble (under the conditions of the experiment) in the solvent in question.

added suitable amounts of water to an acetone solution of cellulose acetate, and collected the precipitate formed after various lengths of time.

(*3*) *Synthetic products:* Whitby *et al.* (301) fractionated polyvinyl acetate in 1928 by diffusion into acetone, and obtained four fractions. In 1930, they (297) extracted polystyrene with each of the solvents ether, acetone, and diethyl oxalate.

In 1929, Staudinger (272) reported the fractionation of polyanethole with ethyl ether, and in another paper (269) that of polyindene with petroleum ether or ethyl ether; the ether-insoluble portion was extracted with boiling cyclohexane, and this solution fractionated by precipitation with methanol.

Zhukov *et al.* (306) in 1935 obtained various fractions of sodium bivinyl polymers by means of petroleum ether, benzene, and chloroform.

C. ULTRACENTRIFUGATION

An ultracentrifuge is an instrument in which sedimentation in centrifugal fields can be measured quantitatively; the centrifugal fields employed are often quite strong, and the apparatus for producing them is rather complex. There are several types of ultracentrifuge in existence, but the earliest and still the best is that developed by Svedberg.

An ultracentrifuge can be used in two different ways: (*1*) to measure sedimentation velocity, that is, the rate of settling of a particle in a given centrifugal field, under standard conditions; (*2*) to measure sedimentation equilibrium, that is, the concentration gradient when equilibrium between sedimentation and diffusion has been established. Method 2 is used for molecular-weight determinations on high polymers; method 1 can be used for molecular-weight determinations also, but its chief value is for the measurement of heterogeneity or polydispersity.

It is obvious from Stokes' law that sedimentation velocity under gravity depends on particle size; the same is true in a centrifugal field, except that the applied force, and therefore the actual velocity, can be controlled, and made large enough to apply to particles of colloidal dimensions. When a strong centrifugal field is applied to a colloidal or a high-polymer solution, which is monodispersed with respect to particle size, the particles will all settle at the same rate; the boundary between solution and pure solvent will move outward from the centre of rotation, and remain sharp (except for slight spreading due to diffusion). In a polydispersed solution, however, the particles will settle at different rates, according to their sizes, and the boundary will spread more and more as it moves down. The amount of spread of the boundary (the concentrations across it are measured by suitable optical means while rotation continues) is a measure of the heterogeneity of the sample; the distribution curve can be obtained by differentiating the curve representing the relationship between the concentration and the distance from the centre.

Evidently, then, the ultracentrifuge furnishes not a preparative, but an analytical, method of fractionation. However, as an analytical method, it is probably one of the best available; Carothers (50), Dostal and Mark (70), Kraemer (149), Mark (176), and Staudinger (268) all recommend it. Kraemer (149) considers fractionation (by solubility methods) far too ineffective and laborious as compared to ultracentrifuge techniques; but the fact remains that an ultracentrifuge is a very complex and specialized piece of equipment, which not every laboratory can obtain. Unlike the above authors, Blease and Tuckett (38) regard fractionation methods as superior to the ultracentrifuge for obtaining distribution curves; they point out how insufficient is the number of ultracentrifuge measurements on record, and emphasize the fact that the validity of the few that there are has been questioned.

Most of the ultracentrifuge measurements on linear high polymers (this does not include the proteins) have been made by Kraemer (148–151). In 1932, Kraemer and Van Natta (151) measured the molecular weights of poly-ω-hydroxydecanoic acids, and found them reasonably, though not entirely, uniform. Later, Kraemer (148, 150) made measurements on cellulose and its derivatives. He pointed out that with the ultracentrifuge, the molecular distribution in cellulose can be easily measured (in cuprammonium) without any of the difficulties experienced in fractionation. His measurements showed that cellulose is continuously heterogeneous or, in other words, that all the members of the homologous polymeric series within a certain range are present. Actually, the calculation of the complete molecular-weight distribution is difficult, and Kraemer proposed the use of the average molecular weight together with a "non-uniformity coefficient" which he defined.

Kraemer's results are in contradiction to those of Stamm (265, 266), who in 1930 had found cellulose to be almost monodispersed, with only a very small proportion of much smaller particles.

Signer and Gross (257, 258) in 1934 performed ultracentrifuge measurements on polystyrene. They encountered a difficulty due to the "matting" of the molecules, that is, chain entanglements preventing the molecules from acting independently. (This difficulty is analogous to that met with in fractional precipitation, when precipitation "en bloc" occurs.)

Lamm (160) in 1934 used the ultracentrifuge to separate starch into two components, corresponding roughly to amylose and amylopectin; each was in turn found to be heterogeneous, especially the amylopectin.

Sebrell (256) mentioned that molecular-weight-distribution measurements by ultracentrifuge on Buna S had been made in the du Pont laboratories, but did not give any details. Scatchard *et al.* (237) in 1944 applied ultracentrifuge measurements to gelatin.[16]

D. CHROMATOGRAPHIC ADSORPTION

Chromatographic adsorption is a useful method for separating mixtures into their components; even closely related substances have often been successfully separated. The method consists in filtering the solution containing the mixture to be separated through a column of an adsorbent, "developing" the chromato-

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[16] For a survey of ultracentrifuge methods and results on high polymers, see Kraemer (6).

gram by washing with pure solvent (this helps to separate the bands further), and eluting various parts of the column separately to recover the adsorbed material. The principle on which the separation is based is preferential adsorption; the components preferentially adsorbed are found in the upper part of the column, those more poorly adsorbed in the lower part, those most poorly adsorbed in the filtrate. Elution reverses the process of adsorption, that is, it causes the substance to pass from the adsorbed layer into solution again; it can be carried out either by filtering the elutant through the column and collecting the filtrates in a series of containers as the bands are washed out of the column one by one, or by dividing the column into bands and eluting each separately. The process received the name "chromatographic" adsorption because of the fact that most substances separated in this way are colored, and the bands in the column are visible; it is possible, however, to separate colorless substances, determining the position and width of the bands by other means, or simply dividing the column arbitrarily into several parts.

Unlike mixtures usually chromatographed, which contain several distinct components, heterogeneous high polymers are continuous mixtures of members of a homologous polymeric series; it is too much to hope to separate each molecular species out of such a mixture. It has been found, however, that the smaller molecules are preferentially sorbed, and that fractionation is therefore possible. The chromatogram is colorless, and as there are no discontinuous bands, but rather a gradual transition from lower to higher fractions, the column is usually divided into an arbitrary number of parts, depending on the number of fractions desired.

The first study of this process as applied to the fractionation of high polymers was made in 1936 by Mark and Saito (179). In an attempt to fractionate cellulose acetate, they tested blood charcoal, aluminum oxide, calcium carbonate, and starch as adsorbents, and acetone and dioxane as solvents; they chose blood charcoal as adsorbent, acetone as solvent, and dioxane as elutant. The process, as finally worked out was as follows: A brass wire net was inserted into a glass tube 3 cm. in diameter and 42 cm. long and filled with three layers of powdered blood charcoal (10 g. each), on top of a bottom layer of glass wool and asbestos; the layers were separated from each other by round pieces of cloth. Three hundred cubic centimeters of a 0.5 per cent solution of cellulose acetate in acetone was filtered through this column under pressure; the chromatogram was washed with acetone, and the filtrate and washings collected. Each layer of charcoal was then dried, well shaken with 50 cc. of dioxane, and after standing for 1 day separated from the solution by filtration through glass wool, asbestos, and starch. The eluate was evaporated at 60°C., and the residue dried. The resulting fractions were found to differ in molecular weight (determined viscometrically), but not in acetyl content.

Loughborough and Stamm (167), in 1936, claimed that fractionation (with respect to molecular weight) of lignin was impossible by filtration through activated charcoal. However, in 1937 Levi and Giera (163) successfully repeated the experiments of Mark and Saito. They found that cellulose diacetate could be chromatographically fractionated; however, with cellulose triacetate, although adsorption is of the same order of magnitude, no fractionation took place. They explained this by assuming that the original cellulose is homogeneous, as is also the triacetate prepared from it, but in the transition from the triacetate to the diacetate, partial depolymerization takes place, resulting in heterogeneity; this would invalidate all methods of fractionating cellulose which depend on acetylation. They also recommended the use of 2:1 ether–alcohol as a solvent for the chromatographic fractionation of cellulose nitrate, with blood charcoal as adsorbent. In 1938, Levi *et al.* (164) compared these chromatographic experiments with fractional precipitation methods; they found an agreement for the cellulose diacetate, but the triacetate could be fractionated by precipitation, while it could not by chromatographic adsorption; they explained this by assuming degradation during precipitation, and particularly during the drying of precipitates.

Cajelli (48) in 1939 described a fractionation of rubber by chromatographic adsorption. Two hundred fifty cubic centimeters of a 0.5 per cent solution in 80:20 benzene-alcohol (95 per cent) was chromatographed in 30 g. of dried animal charcoal; this was washed with the same solution of benzene and alcohol. The charcoal was divided into three approximately equal parts, and each was Soxhlet-extracted with a 50:50 carbon disulfide–carbon tetrachloride solution. After partial evaporation of the resulting solutions at room temperature under vacuum, the viscosities were measured and found to differ.

E. ULTRAFILTRATION

It is often possible to separate particles of different sizes by ultrafiltration through carefully graded cellulose or nitrocellulose membranes. This separation is based on sieving action; the pore sizes are chosen in such a way that particles up to a certain size can pass, but larger ones cannot. This is satisfactory enough with spherical particles, even though complications may occur when the membrane interacts with the solution and passage through the membrane takes place in ways other than by sieving action. But linear particles, such as the high-polymer molecules, even though of colloidal dimensions in one direction, are of molecular dimensions in the other; as long particles have the same width as short ones, they should find it equally easy to pass through the pores of the membranes. However, because of the coiling up of the chains, and internal Brownian motion, long molecules may find it more difficult to pass through the tortuous passages than shorter ones would.

Ultrafiltration has been used with success for the fractionation of cellulose derivatives (35, 36, 47, 73, 74, 153). The method was applied to nitrocellulose by Kumichel (153) in 1928 and by Duclaux and Nodzu (73) in 1929, and to cellulose acetate by Caille (47) in 1931. Many others reject it as too slow, and Meyer (12) considers it unsatisfactory for chain polymers.

F. MOLECULAR DISTILLATION

This last method to be discussed is useful more for the purification of a high polymer (that is, the removal of low-molecular-weight material) than for the separation of high-molecular-weight fractions. In any polymerization or polycondensation reaction, however, molecules all the way from unreacted monomer up to those in the high-molecular-weight range are formed, and, in a sense, the removal of the low-molecular-weight material is a fractionation.

Molecular distillation is essentially a distillation at very low pressure, 10^{-3} or 10^{-6} mm. of mercury. The distance between the distilling pan and the collecting plate is shorter than the mean free path of the evaporating molecules, so that they suffer (on the average) no collisions while in the vapor state. Under these conditions, even very slightly volatile substances can be distilled without decomposition. Moreover, the diffusion velocity of a molecule is inversely proportional to the square root of the molecular weight, so that the lighter molecules distil off first, leaving the residue purified. Even very similar molecules or atoms (homologues or isotopes) can be separated.[17]

Bailey (29) in 1940 used molecular distillation to prove the heterogeneity of lignin. He used temperatures of 75–80°C. and a pressure of 10^{-3} mm. of mercury, and in some cases a temperature of 220°C. and a pressure of 10^{-6} mm. of mercury. He found a difference in the methoxyl content of the fractions.

III. CONCLUSION

Many methods have been used for the fractionation of high-polymeric substances, but some are much more generally useful than others. In order to make this review as helpful as possible, an attempt has been made to mention all the applications of fractionation techniques described in the literature up to the end of 1944.[18] There is no doubt that a few have been missed, but nevertheless the relative amount of space devoted to each method should be a good measure of its popularity. It is evident at once that solubility methods have been much the most frequently used. Of these fractional precipitation, in spite of disadvantages which have frequently been emphasized, is still the most popular, and fractional solution is its closest rival. The general preference for these methods is understandable, for they are relatively convenient, adaptable, versatile, and inexpensive. They are not, however, adequate for all needs.

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[17] See Mark and Raff (10) for a diagram and description of the apparatus. For a survey of various forms of molecular-distillation apparatus see Hickman (Chem. Rev. **34**, 51–106 (1944)).

[18] Since this time other papers dealing with fractionation have, of course, been published. No thorough search for them has been made, but the reader might appreciate having his attention called to the contributions to the theory of fractionation of Scott (and Magat) (J. Chem. Phys. **13**, 172–7, 178–87 (1945)) and of Zimm (Polymer Bull. **1**, 53–9 (1945)); to the discussions of analytical methods in papers by Morey and Tamblyn (J. Applied Phys. **16**, 419–24 (1945)), Doty, Zimm, and Mark (J. Chem. Phys. **13**, 159–66 (1945)), Boyer and Heidenreich (J. Applied Phys. **16**, 621–39 (1945)), and Stern, Senger, and Davis (Polymer Bull. **1**, 31–9 (1945)); and to the studies of preparative methods described by Howlett and Urquhart (Shirley Institute Memoirs **19**, 79–102 (1945)), Tamblyn, Morey, and Wagner (Ind. Eng. Chem. **37**, 573–7 (1945)), Badgley, Frilette, and Mark (Ind. Eng. Chem. **37**, 227–32 (1945)), Hauser, le Beau, and Shen (Rubber Age (N. Y.) **58**, 59–65 (1945)), Morey and Tamblyn (J. Phys. Chem. **50**, 12–22 (1946)), and, in a series of papers on fractionation by coacervation, by Dobry, Gavoret, and Duclaux (J. chim. phys. **42**, 41–4, 92–7, 109–13 (1945)).

Other methods, some of them demanding special techniques and elaborate apparatus, have been devised and found to possess peculiar advantages. When these methods are further improved and other new ones are developed (as they will be), the solubility methods may well lose their present favored position. In particular, it may be safely predicted that less tedious methods will be worked out for obtaining a knowledge of the distribution of molecular weights in a polymer. In the meantime, however, it is still true that in selecting a method for a given fractionation, precipitation or solution should first be considered; if these well-developed techniques prove unsuitable, another method may then be adapted to the particular problem in hand.

Although further advances in the techniques of fractionation may confidently be expected, so much experience has already accumulated that there is now little excuse for neglecting this essential part of the study of a high-polymeric system. If future investigators in the field of high polymers are careful to work with samples that are either homogeneous (monodispersed) or of known heterogeneity, their conclusions will be much more valid than are those in much of the earlier literature.

IV. SUMMARY

Methods that have been used for the fractionation of natural and synthetic high polymers (other than the globular proteins) have been discussed, as follows: fractional precipitation, fractional solution, differential rate of solution, ultracentrifugation, chromatographic adsorption, ultrafiltration, and molecular distillation. A review of the literature to the end of 1944 has been made; and the applications of the various methods have been described in the text and summarized in separate tables.

We should like to express our appreciation to all those who have helped in one way or another in the preparation of this review, particularly to E. D. Maher, A. G. Newcombe, D. H. Simpson, D. A. Henderson, and L. M. Faichney.

V. REFERENCES

Books

(1) BUSSE, W. F.: In *The Chemistry and Technology of Rubber*, C. C. Davis and J. T. Blake (*Editors*), p. 223. Reinhold Publishing Corporation, New York (1937).

(2) FISHER, H. L., AND GERKE, R. H.: In *The Chemistry and Technology of Rubber*, p. 126. Reinhold Publishing Corporation, New York (1937).

(3) HAUSER, E. A.: *Latex*, pp. 52–72. T. Steinkopff, Dresden (1927).
HAUSER, E. A.: *The Colloid Chemistry of the Rubber Industry.* Oxford University Press, London and New York (1928).

(4) HILDEBRAND, J. H.: *The Solubility of Non-electrolytes*, 2nd edition, p. 73. Reinhold Publishing Corporation, New York (1936).

(5) HUGGINS, M. L.: In *High Polymers. Vol. V. Cellulose and Cellulose Derivatives*, E. Ott (*Editor*), pp. 893–909. Interscience Publishers, Inc., New York (1943).

(6) KRAEMER, E. O.: In *The Chemistry of Large Molecules*, R. E. Burk and O. Grummitt (*Editors*), pp. 95–124. Interscience Publishers, Inc., New York (1943).

(7) Mark, H.: *High Polymers. Vol. II. Physical Chemistry of High Polymeric Systems*, pp. 249–51. Interscience Publishers, Inc., New York (1940). (Mark is here summarizing the work of K. H. Meyer and A. J. A. van der Wyk (Helv. Chim. Acta **20**, 1321 (1937)).

(8) Reference 7, pp. 62, 286.

(9) Reference 7, p. 71 *et seq.*

(10) Mark, H., and Raff, R.: *High Polymers. Vol. III. High Polymeric Reactions. Their Theory and Practice*, p. 47. Interscience Publishers, Inc., New York (1941).

(11) Meyer, K. H.: *High Polymers. Vol. IV. Natural and Synthetic High Polymers*, p. 4. Interscience Publishers, Inc., New York (1942).

(12) Reference 11, p. 20.

(13) Reference 11, pp. 121–2.

(14) Reference 11, pp. 571–5.

(15) Purves, C. B.: In *High Polymers. Vol. V. Cellulose and Cellulose Derivatives*, E. Ott (*Editor*), pp. 88–100. Interscience Publishers, Inc., New York (1943).

(16) Spurlin, H. M.: In *High Polymers. Vol. V. Cellulose and Cellulose Derivatives*, E. Ott (*Editor*), pp. 930–42. Interscience Publishers, Inc., New York (1943).

(17) Staudinger, H.: *Die hochmolekularen organischen Verbindungen.* J. Springer, Berlin (1932). Photo-lithoprint reproduction, Edwards Brothers, Inc., Ann Arbor, Michigan (1943)).

(18) Reference 17, p. 7.

(19) Reference 17, p. 10.

(20) Reference 17, p. 161.

(21) Reference 17, pp. 187–8.

(22) Reference 17, pp. 442–3.

(23) Whitby, G. S.: In *The Chemistry and Technology of Rubber*, C. C. Davis and J. T. Blake (*Editors*), pp. 99–100. Reinhold Publishing Corporation, New York (1937).

Periodicals

(24) Abel, G., and Hess, K.: Cellulosechem. **16**, 78–9 (1935).

(25) Adams, H. E., and Powers, P. O.: Ind. Eng. Chem., Anal. Ed. **15**, 711–14 (1943).

(26) Alfrey, T., Bartovics, A., and Mark, H.: J. Am. Chem. Soc. **64**, 1557–60 (1942).

(27) Alfrey, T., Bartovics, A., and Mark, H.: J. Am. Chem. Soc. **65**, 2319–23 (1943).

(27a) Atchison, J. E.: Paper Trade J. **116**, No. 22, 23–34 (1943).

(28) Atsuki, K., and Okajima, S.: J. Soc. Chem. Ind. Japan **39**, Suppl. binding, 57–8 (1936).

(29) Bailey, A.: Paper Trade J. **111**, 27–30 (1940).

(30) Baker, W. O., Fuller, C. S., and Heiss, J. H., Jr.: J. Am. Chem. Soc. **63**, 2142–8 (1941).

(31) Bartovics, A., and Mark, H.: J. Am. Chem. Soc. **65**, 1901–5 (1943).

(32) Bary, P., and Hauser, E. A.: Kautschuk **4**, 96–102 (1928).

(33) Bary, P., and Hauser, E. A.: Rev. gén. caoutchouc **1928**, No. 42, 3–11; Chem. Abstracts **22**, 4005 (1928); Rubber Age (N. Y.) **23**, 685–8 (1928); Chem. Abstracts **22**, 4870 (1928); Rubber Chem. Tech. **1**, 401–9 (1928); Chem. Abstracts **23**, 2067 (1929).

(34) Beadle, C., and Stevens, H. P.: J. Soc. Chem. Ind. **31**, 1099–1103 (1912).

(35) Beck, A., Clément, L., and Rivière, C.: Chimie & industrie **24**, 1068–72 (1930).

(36) Berl, E., and Hefter, O.: Cellulosechem. **14**, 65–77 (1933).

(37) Bezzi, S., and Croatto, U.: Atti ist. Veneto sci. **99**, 905–31 (1939–40); Chem. Abstracts **38**, 1356^6 (1944).

(38) Blease, R. A., and Tuckett, R. F.: Trans. Faraday Soc. **37**, 571–80 (1941).

(39) Bloomfield, G. F., and Farmer, E. H.: Trans. Inst. Rubber Ind. **16**, 69–86 (1940); Rubber Chem. Tech. **14**, 1–14 (1941).

(40) Böhringer, H., and Seyfert, H.: Melliand. Textilber. **20**, 353–5 (1939).

(41) Bréguet, A.: Rev. gén. colloïdes **3,** 200–6, 230–5 (1925); Chem. Abstracts **19,** 3590 (1925).

(42) Brønsted, J. N.: Z. physik. Chem., Bodenstein Festband, pp. 257–66 (1931).

(43) Brønsted, J. N., and Volquartz, K.: Trans. Faraday Soc. **36,** 619–24 (1940).

(44) Brownset, T., and Clibbens, D. A.: J. Textile Inst. **32,** T32–44 (1941).

(45) Brownset, T., and Davidson, G. F.: J. Textile Inst. **32,** T25–31 (1941).

(46) Caille, A.: Chimie & industrie **19,** 402–6 (1928).

(47) Caille, A.: Chimie & industrie **25,** 276–85 (1931).

(48) Cajelli, G.: Gomma **3,** 1–7 (1939); Rev. brasil chim. (São Paulo) **8,** 119–21, 161–7; through Rubber Chem. Tech. **12,** 762–73 (1939).

(49) Campbell, H., and Johnson, P.: Trans. Faraday Soc. **40,** 221–33 (1944).

(50) Carothers, W. H.: Trans. Faraday Soc. **32,** 39–53 (1936).

(51) Caspari, W. A.: J. Soc. Chem. Ind. **32,** 1041–3 (1913).

(52) Caspari, W. A.: J. Chem. Soc. **107,** 162–71 (1915).

(53) Clément, L., and Rivière C.: Bull. soc. chim. [5] **1,** 1075–82 (1934).

(54) Coltof, W.: J. Soc. Chem. Ind. **56,** T363–75 (1937).

(55) Coppick, S., Battista, O. A., and Lytton, M. R.: Division of Cellulose Chemistry of the American Chemical Society, 106th Meeting, Pittsburgh, Pa., September, 1943; Gibson Island Symposium on High Polymers, American Association for the Advancement of Science, Gibson Island, Maryland, July, 1944.

(56) Coppick, S., and Jahn, E. C.: Ind. Eng. Chem. **35,** 890–4 (1943).

(57) Craik, J., and Miles, F. D.: Trans. Faraday Soc. **27,** 756–67 (1931).

(58) Daneš, V. Z.: Kolloid-Z. **68,** 110–15 (1934).

(59) Danilov, S. N., Gol'dfarb, Yu. M., and Zaitseva, E. V.: J. Applied Chem. (U.S.S.R.) **12,** 85–98 (in French, 98) (1939); Chem. Abstracts **33,** 6587^8 (1939).

(60) Davidson, G. F.: J. Textile Inst. **25,** T174–96 (1934).

(61) Davidson, G. F.: J. Textile Inst. **27,** T112–30 (1936).

(62) Deschiens, M.: Chimie & industrie **20,** 1023–33 (1928).

(63) Dobry, A.: J. chim. phys. **31,** 568–76 (1934).

(64) Dobry, A.: J. chim. phys. **32,** 50–7 (1935).

(65) Dobry, A.: Bull. soc. chim. [5] **2,** 1882–4 (1935).

(66) Dobry, A., and Duclaux, J.: Compt. rend. **197,** 1318–20 (1933).

(67) Dobry, A., and Schwob, A.: Bull. soc. chim. [5] **3,** 1790–4 (1936).

(68) Dolmetsch, H., and Reinecke, F.: Zellwolle u. Deut. Kunstseiden-Ztg. **5,** 219–27 (1939).

(69) Dolmetsch, H., and Reinecke, F.: Zellwolle u. Deut. Kunstseiden-Ztg. **5,** 299–307 (1939); Chem. Abstacts **34,** 1167^9 (1940).

(70) Dostal, H., and Mark, H.: Naturwissenschaften **24,** 796 (1936); Trans. Faraday Soc. **33,** 350–3 (1937).

(71) Douglas, S. D., and Stoops, W. N.: Ind. Eng. Chem. **28,** 1152–5 (1936).

(72) Duclaux, J., and Barbière, J.: Bull. soc. chim. [4] **53,** 564–5 (1933).

(73) Duclaux, J., and Nodzu, R.: Rev. gén. colloïdes **7,** 241–50 (1929); Chem. Abstracts **24,** 721 (1930).

(74) Duclaux, J., and Wollman, E.: Bull. soc. chim. **27,** 414–20 (1920).

(75) Eisenhut, O.: Zellwolle u. Deut. Kunstseiden-Ztg. **5,** 261–5 (1939); Melliand Textilber. **20,** 625–30 (1939); Angew. Chem. **52,** 568–72 (1939); Chem. Abstracts **34,** 1182^5, 3097^6 (1940).

(76) Ekenstam, A. af: Svensk Papperstidn. **45,** No. 5, 81–9 (1942) (German and English summaries); Chem. Abstracts **36,** 6339^4 (1942).

(77) Elöd, E., and Schmid-Bielenberg, H.: Z. physik. Chem. **B25,** 27–51 (1934).

(78) Elöd, E., and Schrodt, A.: Z. angew. Chem. **44,** 933–5 (1931).

(79) Engler and Herbst: Ladenburg's *Handwortbuch der Chemie* **5,** 479 (1887); cited by G. S. Whitby (Trans. Inst. Rubber Ind. **6,** 40 (1930)).

(80) Erbring, H.: Kolloid-Z. **90,** 257–68 (1940); Chem. Abstracts **34,** 4325^4 (1940).

(81) Erbring, H., and Sakurada, K.: Kolloid-Z. **73**, 191–201 (1935).
(82) Erbring, H., and Wenstöp, K.: Kolloid-Z. **85**, 342–50 (1938).
(83) Evans, H. C., and Young, D. W.: Ind. Eng. Chem. **34**, 461–6 (1942).
(84) Feuchter, H.: Kolloidchem. Beihefte **20**, 434–48 (1925).
(85) Fink, H., Stahn, R., and Matthes, A.: Z. angew. Chem. **47**, 602–7 (1934).
(86) Flory, P. J.: J. Am. Chem. Soc. **58**, 1877–85 (1936).
(87) Flory, P. J.: J. Am. Chem. Soc. **62**, 1561–5 (1940).
(88) Flory, P. J.: J. Chem. Phys. **9**, 660–1 (1941).
(89) Flory, P. J.: J. Chem. Phys. **10**, 51–61 (1942).
(90) Flory, P. J.: J. Am. Chem. Soc. **65**, 372–82 (1943).
(91) Flory, P. J.: J. Chem. Phys. **12**, 114–15 (1944).
(92) Flory, P. J.: J. Chem. Phys. **12**, 425–38 (1944).
(93) Freundlich, H., and Hauser, E. A.: Kolloid-Z., Zsigmondy Festschrift, pp. 15–36 (1925).
(94) Fuchs, W. M.: J. Am. Chem. Soc. **58**, 673–80 (1936).
(95) Fuoss, R. M.: J. Am. Chem. Soc. **63**, 2401–9 (1941).
(96) Fuoss, R. M., and Mead, D. J.: J. Phys. Chem. **47**, 59–70 (1943).
(97) Gee, G.: Trans. Faraday Soc. **36**, 1171–8 (1940).
(98) Gee, G.: Trans. Faraday Soc. **38**, 108–9 (1942).
(99) Gee, G.: Trans. Faraday Soc. **38**, 276–84 (1942).
(100) Gee, G.: Ann. Repts. Progress Chem. (Chem. Soc. London) **39**, 7–35 (1942).
(101) Gee, G.: Trans. Inst. Rubber Ind. **18**, 266–81 (1943); Rubber Chem. Tech. **16**, 818–33 (1943).
(102) Gee, G.: Trans. Faraday Soc. **40**, 463–80 (1944).
(103) Gee, G., and Treloar, L. R. G.: Trans. Inst. Rubber Ind. **16**, 184–97 (1940); Rubber Chem. Tech. **14**, 580–9 (1941).
(104) Gee, G., and Treloar, L. R. G.: Trans. Faraday Soc. **38**, 147–65 (1942); Rubber Chem. Tech. **16**, 89–110 (1943).
(105) Gehman, S. D., and Field, J. E.: Ind. Eng. Chem. **30**, 1031–6 (1938).
(106) Gladstone and Hibbert: J. Chem. Soc. **53**, 679 (1888); cited by W. F. Busse in *The Chemistry and Technology of Rubber*, C. C. Davis and J. T. Blake (*Editors*), pp. 222, 235 (reference 151). Reinhold Publishing Corporation, New York (1937).
(107) Glikman, S. A.: J. chim. phys. **31**, 458–68 (1934).
(108) Glikman, S. A.: Plasticheskie Massy **1934**, No. 1, 20–24; Chem. Abstracts **28**, 6301^5 (1934).
(109) Glikman, S. A.: J. Phys. Chem. (U.S.S.R.) **5**, 885–93 (1934); Chem. Abstracts **29**, 2820^6 (1935).
(110) Glikman, S. A.: Narodnyĭ Komissariat Tyazheloĭ Prom. S.S.S.R., Nauch.-Issledovatel. Inst. Plasticheskikh Mass., Plasticheskie Massy, Sbornik **2**, 3–30 (1937); Chem. Abstracts **31**, 4108^4 (1937).
(111) Glikman, S. A.: Kunststoffe **25**, 25–9 (1935).
(112) Glikman, S. A.: Kunststoffe **25**, 120–3 (1935).
(113) Glikman, S. A.: Kolloid-Z. **76**, 84–95 (1936).
(114) Hall, C. E., Hauser, E. A., le Beau, D. S., Schmitt, F. O., and Talalay, P.: Ind. Eng. Chem. **36**, 634–40 (1944).
(115) Hauser, E. A.: Ind. Eng. Chem. **21**, 249–51 (1929).
(116) Herington, E. F. G., and Robertson, A.: Trans. Faraday Soc. **38**, 490–501 (1942).
(117) Herz, W.: Cellulosechem. **15**, 95–9 (1934).
(118) Herz, W.: Cellulosechem. **16**, 56 (1935).
(119) Herzog, R. O., and Deripasko, A.: Cellulosechem. **13**, 25–31 (1932).
(120) Hess, K., and Ulmann, M.: Ber. **67B**, 2131–45 (1934).
(121) Huggins, M. L.: J. Chem. Phys. **9**, 440 (1941).
(122) Huggins, M. L.: J. Phys. Chem. **46**, 151–8 (1942).
(123) Huggins, M. L.: Ann. N. Y. Acad. Sci. **43**, 1–32 (1942).

(124) Huggins, M. L.: J. Am. Chem. Soc. **64**, 1712–19 (1942).

(125) Huggins, M. L.: Ind. Eng. Chem. **35**, 216–20 (1943).

(126) Huggins, M. L.: J. Applied Phys. **14**, 246–8 (1943).

(127) Huggins, M. L.: Ann. N. Y. Acad. Sci. **44**, 431–3 (1943).

(128) Hulburt, H. M., Harman, R. H., Tobolsky, A. V., and Eyring, H.: Ann. N. Y. Acad. Sci. **44**, 371–418 (1943).

(129) Husemann, E.: J. prakt. Chem. **158**, 163–75 (1941); Chem. Abstracts **36**, 18^2 (1942).

(130) Iwasaki, S.: J. Soc. Chem. Ind. Japan **34**, Suppl. binding 9–10 (1931).

(131) Jirgensons, Br.: J. prakt. Chem. **159**, 303–12 (1942); Chem. Abstracts **37**, 3772^9 (1943).

(132) Jirgensons, Br.: J. prakt. Chem. **160**, 21–32 (1942); Chem. Abstracts **37**, 4292^2 (1943).

(133) Jirgensons, Br.: J. prakt. Chem. **160**, 65–73 (1942); Chem. Abstracts **37**, 3773^6 (1943).

(134) Jirgensons, Br.: Biochem. Z. **310**, 325–34 (1942); Chem. Abstracts **37**, 4292^4 (1943).

(135) Jirgensons, Br.: Biochem. Z. **311**, 332–46 (1942); Chem. Abstracts **37**, 4749^8 (1943).

(136) Jirgensons, Br.: Kunststoff-Tech. u. Kunststoff.-Anwend. **12**, 279–86 (1942); Chem. Abstracts **38**, 5128^6 (1944).

(137) Jirgensons, Br.: J. prakt. Chem. **161**, 30–48 (1942); Chem. Abstracts **37**, 4604^3 (1943).

(138) Jurisch, I.: Chem.-Ztg. **64**, 269–72 (1940).

(139) Kemp, A. R., and Peters, H.: J. Phys. Chem. **43**, 923–39 (1939); Rubber Chem. Tech. **13**, 28–41 (1940).

(140) Kemp, A. R., and Peters, H.: J. Phys. Chem. **43**, 1063–82 (1939); Rubber Chem. Tech. **13**, 11–27 (1940).

(141) Kemp, A. R., and Peters, H.: Ind. Eng. Chem. **33**, 1391–8 (1941).

(142) Kemp, A. R., and Peters, H.: Ind. Eng. Chem. **34**, 1097–1102 (1942).

(143) Kemp, A. R., and Peters, H.: Ind. Eng. Chem. **34**, 1192–9 (1942).

(144) Kemp, A. R., and Straitiff, W. G.: Ind. Eng. Chem. **36**, 707–15 (1944).

(145) Kern, W., and Fernow, H.: J. prakt. Chem. **160**, 296–314 (1942); through Rubber Chem. Tech. **18**, 267–79 (1945).

(146) Komarov, V. A., and Selivanova, N. P.: Sintet. Kauchuk **1936**, No. 10, 7–10: Chem. Abstracts **31**, 6051^5 (1937).

(147) Kovarskaya, B. M., and Lipatov, S. M.: Colloid J. (U.S.S.R.) **5**, 767–79 (1939); Chem. Abstracts **34**, 3129^7 (1940).

(148) Kraemer, E. O.: Ind. Eng. Chem. **30**, 1200–3 (1938).

(149) Kraemer, E. O.: J. Franklin Inst. **231**, 1–21 (1941).

(150) Kraemer, E. O., and Lansing, W. D.: J. Phys. Chem. **39**, 153–68 (1935).

(151) Kraemer, E. O., and Van Natta, F. J.: J. Phys. Chem. **36**, 3175–86 (1932).

(152) Krüger, D.: Z. angew. Chem. **41**, 407–8 (1928).

(153) Kumichel, W.: Kolloidchem. Beihefte **26**, 161–98 (1928).

(154) Kumichel, W.: Papier-Fabr. **36**, Tech.-Wiss. Tl. 497–508 (1938).

(155) Lachs, H., Kronman, J., and Wajs, J.: Kolloid-Z. **79**, 91–102 (1937).

(156) Lachs, H., Kronman, J., and Wajs, J.: Kolloid-Z. **84**, 199–204 (1938).

(157) Lachs, H., Kronman, J., and Wajs, J.: Przemysl Chem. **22**, 156–71 (English summary, 170–1) (1938).

(158) Lachs, H., Kronman, H., and Zurawicki, I.: Kolloid-Z. **87**, 195–9 (1939).

(159) Lachs, H., and Zurawicki, I.: Przemysl Chem. **22**, 430–3 (English summary, 433) (1938).

(160) Lamm, O.: Kolloid-Z. **69**, 44–56 (1934).

(161) Lampitt, L. H., Fuller, C. H. F., and Goldenberg, N.: J. Soc. Chem. Ind. **60**, 1–6 (1941); Chem. Abstracts **35**, 8340^8 (1941).

(162) Lansing, W. D., and Kraemer, E. O.: J. Am. Chem. Soc. **57**, 1369–77 (1935).

(163) Levi, G. R., and Giera, A.: Gazz. chim. ital. **67**, 719–23 (1937); Chem. Abstracts **32**, 4327^6 (1938).

(164) Levi, G. R., Villotta, U., and Monticelli, M.: Gazz. chim. ital. **68**, 589–92 (1938); Chem. Abstracts **33**, 1492^1 (1939).

(165) Levine, M., Foster, J. F., and Hixon, R. M.: J. Am. Chem. Soc. **64**, 2331–7 (1942).
(166) Liepatoff, S. M., and Putilowa, I. N.: Kolloid-Z. **71**, 83–7 (1935).
(167) Loughborough, D. L., and Stamm, A. J.: J. Phys. Chem. **40**, 1113–32 (1936).
(168) Lovell, E. L., and Hibbert, H.: J. Am. Chem. Soc. **61**, 1916–20 (1939).
(169) Lovell, E. L., and Hibbert, H.: J. Am. Chem. Soc. **63**, 2070–3 (1941).
(170) McBain, J. W., Harvey, C. E., and Smith, L. E.: J. Phys. Chem. **30**, 312–52 (1926).
(171) McNally, J. G., and Godbout, A. P.: J. Am. Chem. Soc. **51**, 3095–3101 (1929).
(172) Mardles, E. W. J.: J. Chem. Soc. **123**, 1951–7 (1923).
(173) Mardles, E. W. J.: J. Soc. Chem. Ind. **42**, 127–136T (1923).
(174) Mardles, E. W. J.: Kolloid-Z. **49**, 4–11, 11–16 (1929).
(175) Margaritov, V. B., and Serebryannikova, L. K.: Colloid J. (U.S.S.R.) **6**, 283–5 (1940); Chem. Abstracts **35**, 3139[1] (1941).
(176) Mark, H.: Paper Trade J. **113**, No. 3, 34–40 (1941); Tech. Assoc. Papers **24**, 217–23 (1941).
(177) Mark, H.: Rayon Textile Monthly **22**, 409–10 (1941).
(178) Mark, H.: Record of Chemical Progress 1–5 (January–April, 1944).
(179) Mark, H., and Saito, G.: Monatsh. **68**, 237–43 (1936).
(180) Mark, H., and Simha, R.: Trans. Faraday Soc. **36**, 611–18 (1940).
(181) Marshall, A.: Zellwolle u. Kunstseide **1**, 117–22 (1943); Chem. Abstracts **38**, 5079[7] (1944).
(182) Medvedev, A. I.: Kunststoffe **23**, 249–51, 273–6 (1933).
(183) Medvedev, A. I., and Denisov, S. V.: J. Applied Chem. (U.S.S.R.) **6**, 880–8 (1933); Chem. Abstracts **28**, 3892[3] (1934).
(184) Melville, H. W.: Trans. Faraday Soc. **40**, 217–20 (1944).
(185) Meyer, K. H.: Helv. Chim. Acta **23**, 1063–70 (1940); Z. physik. Chem. **B44**, 383–91 (1939).
(186) Midgley, T., Jr.: Ind. Eng. Chem. **34**, 891–6 (1942).
(187) Midgley, T., Jr., and Henne, A. L.: J. Phys. Chem. **36**, 2880–4 (1932).
(188) Midgley, T., Jr., and Henne, A. L.: J. Am. Chem. Soc. **59**, 706–7 (1937); Rubber Chem. Tech. **10**, 641–2 (1937).
(189) Midgley, T., Jr., Henne, A. L., and Renoll, M. W.: J. Am. Chem. Soc. **53**, 2733–7 (1931); Rubber Chem. Tech. **4**, 547–51 (1931).
(190) Midgley, T., Jr., Henne, A. L., and Renoll, M. W.: J. Am. Chem. Soc. **54**, 3343–8 (1932).
(191) Midgley, T., Jr., Henne, A. L., and Renoll, M. W.: J. Am. Chem. Soc. **54**, 3381–3 (1932).
(192) Midgley, T., Jr., Henne, A. L., Shepard, A. F., and Renoll, M. W.: J. Am. Chem. Soc. **56**, 1325–6 (1934).
(193) Midgley, T., Jr., Henne, A. L., Shepard, A. F., and Renoll, M. W.: J. Am. Chem. Soc. **57**, 2318–21 (1935).
(194) Montroll, E. W., and Simha, R.: J. Chem. Phys. **8**, 721–7 (1940).
(195) Morey, D. R., and Tamblyn, J. W.: Rubber Age **55**, 375 (1944) (abstract). Inaugural Meeting of Division of High Polymer Physics, Rochester, New York, June, 1944.
(196) Morozov, A. A.: Colloid J. (U.S.S.R.) **5**, 691–706 (1939); Chem. Abstracts **34**, 1180[7] (1940).
(197) Mosimann, H.: Helv. Chim. Acta **26**, 61–75, 369–98 (1943); Chem. Abstracts **37**, 6522[3,5] (1943).
(198) Mosimann, H., and Signer, R.: The Svedberg (Mem. Vol.) **1944**, 464–73; Chem. Abstracts **39**, 1096[9] (1945).
(199) Nagorny, A.: Kolloid-Z. **41**, 123–30 (1927).
(200) Neuenstein, W. von: Kolloid-Z. **43**, 241–9 (1927).
(201) Neumann, R., Obogi, R., and Rogovin, Z. A.: Cellulosechem. **17**, 87–91 (1936).
(202) Northrop, J. H., and Kunitz, M.: J. Gen. Physiol. **10**, 161–77 (1926).

(203) Obogi, R., and Broda, E.: Kolloid-Z. **69**, 172–8 (1934).

(204) O'Dwyer, M. H.: Biochem. J. **31**, 254–7 (1937).

(205) Ohl, F.: Kunstseide **12**, 468–72 (1930); Chem. Abstracts **25**, 4121 (1931).

(206) Ohl, F.: Kunstseide **14**, 3–7 (1932); Chem. Abstracts **26**, 2861 (1932).

(207) Okamura, I.: Cellulosechem. **14**, 135–8 (1933).

(208) Ostwald, Wo.: Kolloid-Z. **41**, 163–9 (1927).

(209) Ostwald, Wo.: Kolloid-Z. **43**, 249–67 (1927).

(210) Ostwald, Wo., and Ortloff, H.: Kolloid-Z. **58**, 215–25 (1932).

(211) Ott, E.: Ind. Eng. Chem. **32**, 1641–7 (1940).

(212) Patterson, R. F., West, K. A., Lovell, E. L., Hawkins, W. L., and Hibbert, H.: J. Am. Chem. Soc. **64**, 2063–70 (1941).

(213) Potts, T. T., and Bridges, F.: Paper-Maker **93**, TS 79–80, 91–94 (1937); Chem. Abstracts **31**, 6875^6 (1937); Proc. Tech. Sect., Paper Makers' Assoc. Gt. Brit. Ireland **18**, Pt. 1B, 325–40 (1937); Chem. Abstracts **32**, 3609^1 (1938).

(214) Pummerer, R.: Kautschuk **2**, 85–8 (1926).

(215) Pummerer, R.: Kautschuk **3**, 233–6 (1927).

(216) Pummerer, R.: Kautschuk **5**, 129–35 (1929).

(217) Pummerer, R., Andriessen, A., and Gündel, W.: Ber. **60B**, 1583–91 (1928); Rubber Chem. Tech. **2**, 367–72 (1929).

(218) Pummerer, R., and Koch, A.: Ann. **438**, 294–313 (1924).

(219) Pummerer, R., and Miedel, H.: Ber. **60B**, 2148–52 (1927).

(220) Pummerer, R., and Miedel, H.: Rubber Chem. Tech. **1**, 163–6 (1928).

(221) Pummerer, R., and Pahl, H.: Ber. **60B**, 2152–63 (1927).

(222) Pummerer, R., and Pahl, H.: Rubber Chem. Tech. **1**, 167–76 (1928).

(223) Rath, H., and Dolmetsch, H.: Klepzig's Textil. Z. **41**, 475–90 (1938).

(224) Rocha, H. J.: Kolloidchem. Beihefte **30**, 230–48 (1930).

(225) Rogovin, Z. A., and Glazman, S.: J. Applied Chem. (U.S.S.R.) **8**, 1237–47 (1935); Chem. Abstracts **30**, 6554^9 (1936); J. Applied Chem. (U.S.S.R.) **9**, 2256–9 (in French, 2259) (1936); Chem. Abstracts **31**, 4492^8 (1937).

(226) Rogovin, Z. A., and Glazman, S.: Kolloid-Z. **76**, 210–13 (1936).

(227) Rogovin, Z. A., and Tsaplina, L.: Colloid J. (U.S.S.R.) **7**, 171–88 (1941); Chem. Abstracts **39**, 1569^9 (1945).

(228) Saito, G.: J. Soc. Chem. Ind. Japan. **43**, Suppl. binding 160–1 (1940).

(229) Sakurada, I.: Ber. **63B**, 2027–42 (1930).

(230) Sakurada, I.: J. Soc. Chem. Ind. Japan **34**, Suppl. binding 426–7 (1931).

(231) Sakurada, I.: Cellulosechem. **13**, 153–5 (1932).

(232) Sakurada, I., and Kido, I.: Cellulose Ind. **9**, 238–46 (in German, 27–33) (1933); Chem. Abstracts **28**, 1184^8 (1934).

(233) Sakurada, I., and Saito, N.: Kolloid-Z. **81**, 208–12 (1937).

(234) Sakurada, I., and Shojino, M.: Kolloid-Z. **68**, 300–5 (1934).

(235) Sakurada, I., and Taniguchi, M.: J. Soc. Chem. Ind. Japan **35**, Suppl. binding 249–53 (1932).

(236) Sakurada, I., and Taniguchi, M.: J. Soc. Chem. Ind. Japan **35**, Suppl. binding 253–6 (1932).

(237) Scatchard, G., Oncley, J. L., Williams, J. W., and Brown, A.: J. Am. Chem. Soc. **66**, 1980–1 (1944).

(238) Schieber, W.: Z. angew. Chem. **52**, 487–8 (1939).

(239) Schieber, W.: Papier-Fabr. **37**, Tech.-Wiss. Tl. 245–50 (1939).

(240) Schieber, W.: Zellwolle u. Deut. Kunstseiden-Ztg. **5**, 266–74 (1939); Chem. Abstracts **34**, 1181^9 (1940).

(241) Schieber, W.: Z. angew. Chem. **52**, 561–8 (1939); Melliand Textilber. **20**, 617–25 (1939); Chem. Abstracts **34**, 3096^3 (1940).

(242) Schulz, G. V.: Z. physik. Chem. **B30**, 379–98 (1935).

(243) Schulz, G. V.: Z. physik. Chem. **B32**, 27–45 (1936).

(244) Schulz, G. V.: Z. physik. Chem. **A179**, 321–55 (1937).

(245) Schulz, G. V.: Z. physik. Chem. **B41**, 466–8 (1938).

(246) Schulz, G. V.: Z. physik. Chem. **B46**, 137–56 (1940); Chem. Abstracts **35**, 953^3 (1941).

(247) Schulz, G. V.: Z. physik. Chem. **B47**, 155–93 (1940); Chem. Abstracts **35**, 953^6 (1941).

(248) Schulz, G. V.: Z. physik. Chem. **B52**, 50–60 (1942); Chem. Abstracts **37**, 5862^5 (1943).

(249) Schulz, G. V., and Dinglinger, A.: Z. physik. Chem. **B43**, 47–57 (1939); Chem. Abstracts **33**, 5732^6 (1939).

(250) Schulz, G. V., and Dinglinger, A.: J. prakt. Chem. **158**, 136–62 (1941); Chem. Abstracts **35**, 7794^4 (1941).

(251) Schulz, G. V., and Husemann, E.: Z. physik. Chem. **B34**, 187–213 (1936).

(252) Schulz, G. V., Husemann, E., and Löhmann, H. J.: Z. physik. Chem. **B52**, 23–49 (1942); Chem. Abstracts **37**, 5862^1 (1943).

(253) Schulz, G. V., and Jirgensons, B.: Z. physik. Chem. **B46**, 105–36 (1940); Chem. Abstracts **35**, 953^1 (1941).

(254) Schulz, G. V., and Löhmann, H. J.: J. prakt. Chem. **157**, 238–82 (1941); Chem. Abstracts **35**, 4589^5 (1941).

(255) Schulz, G. V., and Nordt, E.: J. prakt. Chem. **155**, 115–28 (1940).

(256) Sebrell, L. B.: Ind. Eng. Chem. **35**, 736–50 (1943).

(257) Signer, R., and Gross, R.: Helv. Chim. Acta **17**, 59–77 (1934).

(258) Signer, R., and Gross, H.: Helv. Chim. Acta **17**, 726–35 (1934); *cf.* Signer, R.: Trans. Faraday Soc. **32**, 296–307 (1936).

(259) Signer, R., and Liechti, J.: Helv. Chim. Acta **21**, 530–4 (1938).

(260) Smith, W. H., and Holt, W. L.: J. Research Natl. Bur. Standards **13**, 465–8 (1934).

(261) Smith, W. H., and Saylor, C. P.: J. Research Natl. Bur. Standards **13**, 453–64 (1934).

(262) Smith, W. H., Saylor, C. P., and Wing, H. J.: J. Research Natl. Bur. Standards **10**, 479–92 (1933).

(263) Sookne, A. M., Rutherford, H. A., Mark, H., and Harris, M.: J. Research Natl. Bur. Standards **29**, 123–30 (1942); Am. Dyestuff Reptr. **31**, 417–20 (1942).

(264) Spurlin, H. M.: Ind. Eng. Chem. **30**, 538–42 (1938).

(265) Stamm, A. J.: J. Am. Chem. Soc. **52**, 3047–62 (1930).

(266) Stamm, A. J.: J. Am. Chem. Soc. **52**, 3062–7 (1930).

(267) Staudinger, H.: Trans. Faraday Soc. **32**, 323–35 (1936).

(268) Staudinger, H.: Papier-Fabr. **36**, Tech.-Wiss. Tl. 381–8 (1938).

(269) Staudinger, H., Ashdown, A. A., Brunner, M., Bruson, H. A., and Wehrli, S.: Helv. Chim. Acta **12**, 934–57 (1929).

(270) Staudinger, H., Berger, G., and Fischer, K.: J. prakt. Chem. **160**, 95–119 (1942); Chem. Abstracts **37**, 4047^3 (1943).

(271) Staudinger, H., and Bondy, H. F.: Ber. **63**B, 724–30 (1930); Rubber Chem. Tech. **3**, 511–15 (1930).

(272) Staudinger, H., and Brunner, M.: Helv. Chim. Acta **12**, 972–84 (1929).

(273) Staudinger, H., Brunner, M., Frey, K., Garbsch, P., Signer, R. and Wehrli, S.: Ber. **62B**, 241–63 (1929).

(274) Staudinger, H., and Eder, K.: J. prakt. Chem. **159**, 39–69 (1941); Chem. Abstracts **37**, 3597^6 (1943).

(275) Staudinger, H., Frey, K., and Starck, W.: Ber. **60B**, 1782–92 (1927).

(276) Staudinger, H., and Heuer, W.: Z. physik. Chem. **A171**, 129–80 (1934).

(277) Staudinger, H., and Husemann, E.: Ann. **530**, 1–20 (1937).

(278) Staudinger, H., and Jurisch, J.: Melliand Textilber. **20**, 693–6 (1939).

(279) Staudinger, H., and Reinecke, F.: Ann. **535**, 47–100 (1938); especially pp. 52–3.

(280) Staudinger, H., and Schaal, W.: Helv. Chim. Acta **13**, 1355–60 (1930).

(281) Staudinger, H., and Schweitzer, O.: Ber. **62B**, 2395–2405 (1929).

(282) Stevens, H. P.: J. Soc. Chem. Ind. **38**, 192–6T (1919); Rubber Age (N. Y.) **5**, 527–30 (1919).

(283) Stevens, H. P.: Trans. Inst. Rubber Ind. **16**, 276–81 (1941); Rubber Chem. Tech. **14**, 590–5 (1941); discussion of reference 39.

(284) Strauss, F. L., and Levy, R. M.: Paper Trade J. **114**, No. 18, 33–7 (1942).

(285) Svedberg, The: Svensk Papperstidn. **45**, 444–58 (German and English summaries) (1942); Chem. Abstracts **37**, 2570^3 (1943).

(286) Takei, M., and Erbring, H.: Kolloid-Z. **101**, 59–64 (1942); Chem. Abstracts **38**, 3125^4 (1944).

(287) Tamblyn, J. W., Tichenor, R. L., Morey, D. R., and Wagner, R. H.: Inaugural Meeting of Division of High Polymer Physics, Rochester, New York, June, 1944; Rubber Age (N. Y.) **55**, 375 (1944) (abstract).

(288) Taniguchi, M.: J. Soc. Chem. Ind. Japan **44**, Suppl. binding 85–6 (1941).

(289) Taniguchi, M., and Sakurada, I.: J. Soc. Chem. Ind. Japan **37**, Suppl. binding 485–6 (1934).

(290) Tobolsky, A. V.: J. Chem. Phys. **12**, 402–4 (1944).

(291) Tydén, H.: Svensk. Kem. Tid. **51**, 100–1 (1939) (in German); Chem. Abstracts **33**, 6587^3 (1939).

(292) Uchida, M.: Cellulose Ind. **6**, 253–63 (abstracts 45–6, in English) (1930).

(293) Ulmann, M.: Ber. **68B**, 134–45 (1935).

(294) Ushakov, S. N., Geller, I. M., *et al.*: Plasticheskie Massy, Sbornik Stateĭ **1939**, 30–9; Chem. Abstracts **36**, 3043^9 (1942).

(295) Weber, C. O.: J. Soc. Chem. Ind. **19**, 215–21 (1900).

(296) Weber, C. O.: Ber. **33**, 779–96 (1900).

(297) Whitby, G. S.: Trans. Inst. Rubber Ind. **6**, 40–62 (1930).

(298) Whitby, G. S.: J. Phys. Chem. **36**, 198–214 (1932).

(299) Whitby, G. S., and Katz, M.: Can. J. Research **4**, 344–60 (1930).

(300) Whitby, G. S., and Katz, M.: J. Am. Chem. Soc. **50**, 1160–71 (1928).

(301) Whitby, G. S., McNally, J. G., and Gallay, W.: Trans. Roy. Soc. Canada **22**, III, 27–32 (1928).

(302) Whitby, G. S., McNally, J. G., and Gallay, W.: Colloid Symposium Monograph **6**, 225–36 (1928).

(303) Yamaguchi, B.: Kolloid-Z. **72**, 51–5 (1935).

(304) Yamamoto, S.: Cellulose Ind. **9**, 409 (English abstracts, 1–3) (1933); Chem. Abstracts **27**, 3328 (1933).

(305) Zhukov, I. I., and Komarov, V. A.: Sbornik Trudov Opytnogo Zavoda im. S. V. Lebedeva **1938**, 3–11; Chem. Abstracts **34**, 2643^6 (1940).

(306) Zhukov, I. I., Simkhovich, F. M., Talmud, S. L., and Nikol'skaya, V. P.: Colloid J. (U.S.S.R.) **1**, 16–20 (1935); Chem. Abstracts **30**, 7969^3 (1936).

(307) Zhukov, I. I., Simkhovich, F. M., Talmud, S. L., and Nikol'skaya, V. P.: Sintet. Kauchuk **4**, No. 2, 6–16 (1935); Chem. Abstracts **29**, 4626^8 (1935).

Patents

(308) British Celanese Ltd.: British patent 345,408 (February 7, 1929).

(309) I. G. Farbenindustrie A.-G. (Erich Correns, inventor); German patent 595,390 (April 13, 1934).

(310) Kunc, J., and Miller, F. L. (to Standard Oil Development Company): U. S. patent 2,255,388 (September 9, 1941).

(311) Scheidegger, J. (to Celanese Corporation of America): U. S. patent 1,959,446 (May 22, 1934).

(312) Staud, C. J., and Yackel, E. C. (to Eastman Kodak Company): U. S. patent 2,024,666 (December 17, 1935).