215° was then distilled several times under reduced pressure. The final product had a boiling point of 69–69.5° at 7 mm.

Steroids.—

		M. p., °C.
1.	Cholestanediol-3β,7α	167–168
2.	Cholestanediol-3β,7β	152–153
3.	Cholestanol-3β-one-7	164–165
4.	Δ⁵-Cholestenol-3β-one-7	168–169
5.	Testosterone = Δ⁴-androstenol-17α-one-3	154–155
6.	cis-Testosterone = Δ⁴-androstenol-17β-one-3	220–221
7.	Δ⁵-Androstenediol-3β,17α	182–183
8.	Δ⁵-Androstenediol-3β,17β	198.0–198.5
9.	Androsterone = etio-allo-cholanol-3α-one-17	182.5–183.5
10.	β-Androsterone = etio-allo-cholanol-3β-one-17	171.4–173
11.	Δ⁴-Androstenedione-3,17 = Δ⁴-etio-allo-cholene-dione-3,17	173–174
12.	Dehydroandrosterone = Δ⁵-andro-stenol-3β-one-17	135–137

Compounds 1–4 were obtained from Dr. O. Wintersteiner of the Squibb Institute for Medical Research, compounds 5–11 from Dr. C. R. Scholz, of Ciba Pharmaceutical Products, Inc., and compound 12 from Professor Byron Riegel of Northwestern University.

Summary

The dipole moments of eight androstane derivatives, four sterols, and isophorone have been measured in dioxane solution. The moments of the compounds are as follows: cholestanediol-3β,7α, 2.31; cholestanediol-3β,7β, 2.55; cholestanol-3β-one-7, 2.98; Δ⁵-cholestenol-3β-one-7, 3.79; androsterone, 3.70; β-androsterone, 2.95; Δ⁵-androstenediol-3β,17α, 2.89; Δ⁵-androstenediol-3β,17β, 2.69; Δ⁵-androstenol-3β-one-17, 2.46; testosterone, 4.32; cis-testosterone, 5.17; Δ⁴-androstenedione-3,17, 3.32; isophorone, 3.96.

The moments of four of these compounds fall outside the range calculated for free rotation of the hydroxyl groups, from which it is concluded that the 3β- and 17β-hydroxyl groups do not have freedom of rotation.

A ketone group conjugated with a double bond in a six-membered ring has a moment about 1 unit higher than a simple ketone.

The dipole moment of isophorone indicates that the compound exists chiefly in a form with the double bond conjugated with the ketone group.

A double bond in the sterol nucleus that is not conjugated decreases the moment of the compound by 0.49 unit in the one case studied. Two explanations are discussed.

Sterols with two polar groups and differing only in respect to the position of a hydroxyl group on the same carbon atom have different moments. The difference in moments of the members of any epimeric pair depends somewhat on the moment of the other polar group in the molecule.

There appears to be no correlation between the dipole moments of the sex hormones and their physiological activity.

Gel Formation in Addition Polymerization[1]

BY CHEVES WALLING

When a polymerization is carried out in the presence of a polyfunctional component which permits the three-dimensional growth and cross-linking of chains, there is, at some stage in the reaction, a rather abrupt transition from the liquid to the gel state. In 1931 Carothers pointed out that such a gel is the result of the linking together of polymer molecules into a three-dimensional network of indefinitely large size.[2] In 1941 Flory outlined a general method for determining the extent of reaction at which such a network becomes possible, and carried out the detailed calculations for the case of polycondensation reactions.[3] His results were in good agreement with experiment, and he indicated that a similar

method might be applied to addition polymerizations. Recently, Stockmayer[4] has applied Flory's procedure to a mixture of polyfunctional components with a generalized distribution of functionality and has obtained an expression which should predict the gel-point in both vulcanization reactions and addition polymerizations in which all functions have equal reactivity.

In this paper, calculated and observed gel-points are compared for the systems methyl methacrylate–ethylene dimethacrylate and vinyl acetate–divinyl adipate. Observed extents of reaction at the gel-point are, in general, found to be several times those calculated, particularly in experiments in which very early gel-points are anticipated. This discrepancy is discussed from the point of view of the discontinuous nature of dilute polymer solutions.

(1) Presented before the Physical and Inorganic Section at the New York meeting of the American Chemical Society, September 12, 1944.

(2) W. H. Carothers, *Chem. Rev.*, **8**, 402 (1931).

(3) P. J. Flory, THIS JOURNAL, **63**, 3083 (1941).

(4) W. H. Stockmayer, *J. Chem. Phys.*, **12**, 125 (1944).

Flory's[3] method of calculating the gel-point in a polymerizing system is a statistical one, and consists in determining the conditions under which the existence of an indefinitely large molecule becomes possible. Stated in the most general terms, this possibility arises when the expected number of additional elements to which a randomly selected element, known only to be connected to a single other element or system of elements, is attached exceeds unity. Accordingly, the point in a reaction where this expectation becomes unity is defined as the gel-point.[5] This condition for the formation of infinite networks applies regardless of whether monomer units in general, polyfunctional branching centers, or whole polymer chains are chosen as the elements to be considered.

Paralleling Flory's treatment of polycondensation reactions, the gel-point in the addition polymerization of a mixture of mono- and divinyl monomers[6] in which all vinyl groups have the same reactivity may be calculated as follows. Choosing as the elements in the polymer the monomer units regardless of the number of reacted vinyl groups which they contain, let p equal the probability that a given vinyl group has reacted, q, that a reacted vinyl group ends a chain, and r, that a unit contains two vinyl groups (reacted or unreacted). That p and r are independent probabilities, as the treatment requires, follows from the assumption that all vinyl groups have equal reactivity. The independence of q requires, as well, that the ratio of rates of chain growth to chain transfer or termination is independent of chain length and that each chain is formed by a single active center. In the case of catalyzed polymerizations, where chain transfer with solvent is appreciable, or where termination is by disproportionation rather than coupling, both requirements are probably met satisfactorily. Employing these symbols, the gel condition may be written down as

$$(1 - r)(1 - q) + r\,[(1 - q) + 2p\,(1 - q)] = 1 \quad (1)$$

which simplies to

$$2pr = q/(1 - q) \quad (2)$$

The first product in (1) is the expectation of additional attachments arising from the selection of a monovinyl unit, $(1 - q)$, times the probability that such a unit was chosen, $(1 - r)$. The second product is the expectation arising from the selection of a divinyl unit, $(1 - q)$ from the other end of the reacted vinyl group by which it is known to be already connected, plus $p(1 - q)$ from the other vinyl group which may or may not have re-

(5) For an excellent and detailed discussion of the reasoning behind these statements, the reader is referred to Flory's original paper.[1]

(6) Because, in general, the reaction of a vinyl group in an addition polymerization results in the attachment of the monomer unit to two other units, an n-vinyl monomer (i. e., one containing n reactive vinyl groups) corresponds to a $2n$-functional unit in the polycondensations discussed by Flory. However, as will be seen later, in any statistical consideration of the polymers, these functions should be thought of as reacting in pairs.

acted, times the probability r that a divinyl unit was chosen. The manner in which p appears in the equation is a result of the fact that addition polymerizations are rapid chain reactions, so that in these considerations, when one end of a vinyl group has reacted, the possibility that the other has not may be neglected. This rapidity of chain growth is in direct contrast to the behavior of polycondensation reactions and its consequences will be considered again in this paper in the discussion of experimental results.

If A and B are the concentrations of unreacted mono- and divinyl monomers, A_0 and B_0 their initial concentrations, and all vinyl groups are considered to have the same reactivity, $p = 1 - A/A_0$ (or $1 - (B/B_0)^{1/2}$ by virtue of the fact that B will enter the polymer proportionally twice as fast as A), and $r = 2B_0/(A_0 + 2B_0)$. Noting that $q = 1/\lambda$, the average kinetic chain length in the polymerization (i. e., the average degree of polymerization if all bifunctional units were cut in two between the functions, or the average number of chain growth steps occurring between a transfer or disproportionation reaction), these quantities may be substituted into (2) to yield as the gel-point equation.

$$1 - \frac{A}{A_0} = 1 - \left(\frac{B}{B_0}\right)^{1/2} = \frac{A_0 + 2B_0}{4B_0\,(\lambda - 1)} \quad (3)$$

If the weight average number of units in a kinetic chain is equal to $2\lambda - 1$ (the calculated relationship if chain termination is independent of chain length, and each chain is produced by only one active center[7]), Equation (3) is equivalent to that derived by Stockmayer,[4] employing as branching units the kinetic chains rather than the individual monomer units.[8]

Equation (3) states that the extent of reaction at the gel-point, as measured by $1 - A/A_0$, varies inversely with both the amount of cross-linking agent and the average chain length of the polymerization. In order to test this hypothesis, methyl methacrylate and vinyl acetate have been polymerized in the presence of small amounts of ethylene dimethacrylate and divinyl adipate, respectively. These systems were chosen because it was felt that, in each, the reactivities of all functions should be similar, and because data were available on the viscosity–molecular weight relationship for polymers of both monofunctional monomers.

Experimental

Materials.—Methyl methacrylate and vinyl acetate were commercial materials, fractionated shortly before

(7) Schulz, Z. physik. Chem., **B30**, 379 (1935), using approximations valid only for large values of λ, has obtained 2λ for the weight average number of units. However, when the actual summations are carried out, the above value results.

(8) While the method outlined above stresses the detailed mechanism of addition polymerization with which we are here concerned, the method of Stockmayer seems more general and more elegant in that it predicts the amount of randomly distributed cross-linking necessary to produce gelation in any system when the weight average number of units per chain is known.

use (the former under reduced pressure) and stored in the refrigerator. Ethylene dimethacrylate was prepared by the alcoholysis of methyl methacrylate with ethylene glycol, followed by vacuum distillation. Its physical constants were: b. p. 1 mm., 83–85°, $n^{20}D$ 1.4533. Divinyl adipate was prepared from vinyl acetate and adipic acid.[9] The product boiled at 89.5–89.7° at 0.5 mm. and had $n^{20}D$ '1.4544. Solvents were c. p. materials, used without further purification.

Determinations of gel-points were carried out on approximately 5-cc. samples in 12 × 75 mm. test-tubes, flushed out with nitrogen, corked securely, and placed in a 60° thermostat. From 0.10 to 1.00 g. of benzoyl peroxide per mole of monomers served as catalyst, and gelation occurred in one-half to fifteen hours, depending upon the system. The extent of reaction was followed by index of refraction measurements, the relation being assumed identical with analogous systems containing only the monovinyl monomer, where it was found to be linear. For two experiments containing over 5% of divinyl monomer, the extent of reaction at the gel-point was determined by actual isolation and weighing of the polymer. With the exception of some of the vinyl acetate experiments which showed appreciable induction periods, rates of reaction in any one system were approximately constant and independent of the amount of cross-linking agent. The viscosities of the solutions were determined by inverting the tubes from time to time, and the gel-point taken as the point when a bubble would no longer rise in the solution. The suddenness with which the viscosity rises as the gel-point is approached, particularly when it occurs at a low extent of reaction, is shown in Fig. 1 where the variation in time of bubble rise with extent of reaction is plotted for one of the methyl methacrylate–ethylene dimethacrylate systems. Duplicate experiments usually agreed to better than 10% of the measured values.

Molecular weight determinations by viscosity measurement were carried out on polymer samples prepared by polymerizing pure methyl methacrylate and vinyl acetate under the same conditions as the gelation experiments in order to obtain the values of the average chain length, λ, to use in Equation (3), it being assumed that the small amounts of cross-linking agent employed had no effect on the kinetic chain length. For polymethyl methacrylate in chloroform the relation for unfractionated material determined by Schulz and Dinglinger[10] was used, and for vinyl acetate in acetone that of Staudinger and Warth.[11] Solutions yielding relative viscosities, η_{rel}, of 1.5–2.0 were employed, and the intrinsic viscosity, $[\eta]$, calculated by the equation ln $\eta_{rel}/Cv = [\eta]$. The value at 60° of $[\eta]$ and several values of η_{rel} for the polymer samples in media corresponding to the appropriate reaction mixtures were also measured for calculations which will be discussed below.

Discussion of Results

Results of gelation experiments in which the amount of divinyl monomer is varied between 100 and 0.05%, the average chain length between 400 and 5000, and the amount of solvent from 0 to 67 weight % are listed in Table I. Under these conditions, the gel-point varied from 1.0 to 45% reaction, and inspection indicates that results are in qualitative agreement with Equation (3), with the exception of Experiments 1 and 2, which will be discussed later. Thus, there is a pronounced delay in the gel-point with decreasing amounts of divinyl monomer (compare for example Expts. 3–6) and with decreasing chain length (compare Expts. 3–6 with 7–10). However, when the observed gel-points are compared

(9) Toussaint and MacDowell, U. S. Patent 2,299,862 (1942).
(10) Schulz and Dinglinger, J. prakt. Chem., 158, 136 (1941).
(11) Staudinger and Warth, ibid., 155, 278 (1940).

quantitatively with those calculated from the measured chain lengths and amounts of cross-linking agent, agreement is poor, and it seems reasonable to re-examine the assumptions upon which such derivations are based.
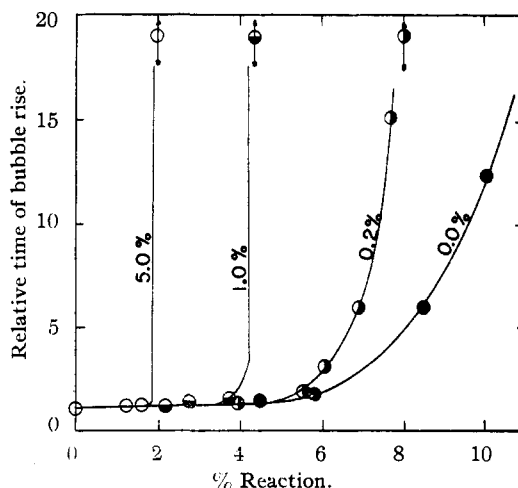

Fig. 1.—Effect of presence of ethylene dimethacrylate upon viscosity (measured by time required for bubble to rise in reaction tube) during polymerization of methyl methacrylate at 60° in presence of 0.1% Bz_2O_2, 1.0% methallyl chloride.

First, if Equation (3) is otherwise correct, observed gel-points should occur slightly later than calculated, because no account has been taken of the occasional formation of cyclic structures. However, there seems to be no a priori reason to assume that the effect would be larger than in the case of polycondensation reactions where it is of minor importance and insufficient to account for discrepancies of the magnitude observed here. Second, the initial assumption that all functions have the same reactivity might be in error. If this were the case, as has been pointed out by Stockmayer, the net result (at least at low extents of reaction) would be merely to introduce a constant before one side of the equation, so that the ratio of observed to calculated gel-points would maintain a constant value. In the last column this ratio is calculated. While the ratio for any amount of cross-linking agent is rather roughly constant (for example, for gel experiments in the presence of 0.05 cross-linking agent it averages 1.62 with an average deviation of 0.55) it varies widely with the amount of cross-linking agent, and at 5% has risen to an average of 13.2. The ratios appear also to be increased somewhat by the presence of solvent. Apparently, the equation, although predicting the gel-point of these systems reasonably well when they contain only very small amounts of cross-linking agent, becomes increasingly inaccurate as the amount of cross-linking agent is increased. The discrepancy in Experiments 1 and 2 containing 100 and 20% cross-linking agent is particularly striking. Al-

TABLE I

CALCULATED AND OBSERVED GEL-POINTS FOR THE SYSTEMS METHYL METHACRYLATE–ETHYLENE DIMETHACRYLATE AND
VINYL ACETATE–DIVINYL ADIPATE

All at 60° in the presence of 0.10 g. benzoyl peroxide/mole unless otherwise noted.

Expt.	Wt. % solvent	Mole % divinyl monomer	λ	% Reaction at gel-point Obs.	Calcd.	Obs./calcd.
Methyl Methacrylate–Ethylene Dimethacrylate						
1	None	100	(?)	2.9	0.022 (?)	132 (?)
2	None	20	(?)	1.3	0.04 (?)	32.5 (?)
3	None	5.0	4860	1.0	0.11	9.10
4	None	1.0		2.25	0.57	3.95
5	None	0.2		5.6	2.8	2.00
6	None	0.05		12.5	11.0	1.14
7[a]	None	5.0		2.0	0.26	7.70
8[a]	None	1.0	2320	4.3	1.2	3.85
9[a]	None	0.2		9.0	6.0	1.50
10[a]	None	0.05		25	24	1.04
11	50	C_6H_6	5.0		1.8	0.17	10.6
12	50	C_6H_6	1.0	3680	3.4	0.72	4.72
13	50	C_6H_6	0.2		9.4	3.9	2.41
14	50	C_6H_6	0.05		35	16	2.20
15	67	C_6H_6	5.0		2.7	0.20	13.5
16	67	C_6H_6	1.0	2810	4.4	0.96	4.59
17	67	C_6H_6	0.2		10.9	5.2	2.00
18	50	EtOAc	5.0		3.7	0.17	21.7
19	50	EtOAc	1.0	3510	5.4	0.75	7.20
20	50	EtOAc	0.2		11.1	4.0	2.78
21	50	EtOAc	0.05		35	17	2.10
22	67	EtOAc	5.0		4.8	0.22	21.8
23	67	EtOAc	1.0	2640	10.7	1.0	10.7
24	67	EtOAc	0.2		20.0	5.3	3.75
25[b]	50	CCl₄	5.0		4.5	0.35	12.8
26[b]	50	CCl₄	1.0	1700	7.1	1.7	4.17
27[b]	50	CCl₄	0.2		30	8.0	3.75
Vinyl Acetate–Divinyl Adipate						
28	None	5.0		2.3	0.14	16.4
29	None	1.0	4300	4.5	0.61	7.38
30	None	0.2		12.5	3.0	4.17
31[b]	50	CH_3COCH_3	5.0		13.8	1.5	9.2
32[b]	50	CH_3COCH_3	2.0	400	21.5	3.4	6.30
33[b]	50	CH_3COCH_3	1.0		45	7.0	6.44

[a] 1% Methallyl chloride added as regulator.   [b] 1.0 g. Bz_2O_2/mole.

though it cannot be assumed that the kinetic chain lengths λ obtained with methyl methacrylate and ethylene dimethacrylate are identical under the same conditions, they are probably of the same order of magnitude. On the other hand, calculating λ from the observed gel-point of Experiment 1 gives a value of about 40, or 1/100 that observed with methyl methacrylate. Apparently Stockmayer's suggestion that the gel-point be used as a quantitative measure of chain length[4] does not hold in the presence of much cross-linking agent. A third and more fundamental assumption made in all derivations of this type is that the medium in the neighborhood of a polymerizing molecule may be treated as if, on the average, it were a continuum having the properties of the solution as a whole. Such a treatment

appears to be justified for a polycondensation reaction where a chain continues to grow during the entire reaction-time and during its life is able to diffuse about through the solution. On the other hand, as noted earlier, addition polymerizations are fast chain reactions so that, once a chain starts, it reacts very rapidly and probably completes its growth in a fraction of a second, reacting only with those molecules which happen to be in the very close vicinity at that moment. If this is the difficulty, it should be reasonable to approach the problem from a fresh point of view, emphasizing this rapidity of chain growth and applicable particularly to systems gelling at low extents of reaction where the previous theory fails most seriously.

To consider the chain growth process early in

the course of the polymerization, it is necessary to adopt some sort of a picture of physical state of a dilute polymer solution. Here it is convenient to turn to information gained through studies of the rheological properties of such solutions. Unfortunately, these properties have been interpreted from the divergent points of view that they are due to the polymer molecules existing as rigid rods,[12] as randomly kinked molecules[13] and as swollen spheres.[14] Without entering into the controversy, it is easiest to discuss the problem from the point of view of the last interpretation and to picture the reaction mixture as consisting of polymer molecules as discrete masses, highly swollen by, and floating in, the solvent. Considering these masses as spheres, their swelling factor (ratio of swollen to unswollen volumes) varies from unity to several hundred.[14,15] It increases with the chain length, λ,[14] and with the solvent properties of the medium,[16] and decreases with increasing polymer concentration.[14,17] As polymerization proceeds, new spheres are continually generated and grow to full size at a rate which is rapid compared with the rate at which they diffuse through the reaction medium. Cross-linking of polymer molecules generally occurs by a growing sphere becoming attached to one which is already formed, and, under the conditions assumed, can only occur between spheres within touching distance at the instant when one is in the process of growth. Obviously, the number of spheres touched by a growing sphere will be a function of the volume fraction, C_v, of the reaction medium filled by the swollen spheres (if all spheres are of the same size, the average number touched can be shown to be $8C_v$, or $7C_v$, depending upon whether or not an active center may arise inside an already existent sphere).[20]

Since any factor which increases either C_v or the probability that the contact between a polymer molecule and an active center leads to cross-linking also increases the prospects for gelation, it is possible by means of the foregoing picture to account qualitatively for all the major trends shown in Table I. The sensitivity of gel-point to chain length (which alters C_v by changing the swelling factor) and to the amount of cross-linking agent (which affects the probability of cross-linking to a touched sphere) has been noted and is in the proper direction. As well, it is to be expected that gel-points will be delayed by dilution with an inert solvent, even if chain length is not affected.

(12) Staudinger and Staiger, *Ber.*, **68**, 707 (1935).

(13) Huggins, *J. Phys. Chem.*, **42**, 911 (1938); **43**, 439 (1939).

(14) Eilers, *Kolloid-Z.*, **102**, 154 (1943).

(15) Kraemer, Chapter XX of Taylor's "Treatise on Physical Chemistry," 2nd edition, D. Van Nostrand Company, New York. N. Y., 1931.

(16) Alfrey, Bartovics and Mark, THIS JOURNAL, **64**, 1557 (1942).

(17) The qualitative conclusions which are reached below are probably equally valid on the basis of a solution of kinked chains or rods (or ellipsoids) in which the variation of swelling factor is replaced by variations in the degree of kinking or of axial ratios. It is only when a quantitative calculation is attempted that a definite choice must be made.

Further, substitution of a poor solvent for a good one, with a resulting reduction in the swelling factor, will delay gelation still further. The effect of dilution is confirmed by a general comparison of the ratios of observed to calculated gel-points in the presence and absence of solvent, and the effect of change of solvent by these ratios in the polymerization of the methyl methacrylate system diluted with carbon tetrachloride or benzene (fairly good solvents) with these ratios in polymerizations of the same system diluted with ethyl acetate (a poor solvent), particularly in the presence of much divinyl monomer.

As the probability of cross-linking is a function primarily of C_v and the amount of divinyl monomer, it might be expected that, if sufficient divinyl monomer is present to ensure cross-linking with practically every touching sphere, all systems should gel at approximately the same value of C_v. Since increasing the amount of divinyl monomer beyond 5% no longer produces earlier gelation, it seems likely that 5% represents the amount necessary to ensure cross-linking with a touching polymer molecule.[18] Figure 1 showed that, in the one system studied, the presence of cross-linking agent does not affect the viscosity of the reaction mixture until the gel-point is approached. Consequently, it should be possible to calculate C_v for systems up to immediately before gelation by using relative viscosities measured on systems containing no cross-linking agent in Eilers' empirical equation[14]

$$\eta_{rel} = \left(\frac{1 - 0.1\ C_v}{1 - 1.35\ C_v}\right)^2 \qquad (4)$$

Results of such measurements, described in the experimental part, are given in Table II. Despite the wide range in extents of reaction at the gel-point, it will be noted that all values of C_v lie between 25 and 46%, in good support of prediction.

TABLE II

η_{rel} AND C_v FOR SOLUTIONS OF MONOFUNCTIONAL MONO-MERS AT CONVERSIONS CORRESPONDING TO GEL-POINTS IN PRESENCE OF 5 MOLE % CROSS-LINKING AGENT

Expt.[a]	Reaction at gel-point, %	η_{rel}	C_v, %
3	1.0	3.9	38
7	2.0	3.7	37
11	1.8	2.9	32
15	2.7	2.3	25
18	3.7	4.8	41
22	4.8	3.0	34
25	4.5	3.5	36
28	2.3	6.0	46
31	13.8	3.7	37

[a] Same as Table I.

(18) By this interpretation, the observed *increase* in extent of reaction at gelation in the presence of 20 and 100% cross-linking agent compared with that in the presence of 5% must be due to a decrease in the swelling factor, either because of shorter chain length or because the growing polymer chain undergoes so many cross-linking reactions with itself that its ability to swell is reduced.

If certain simplifying assumptions are made, a statistical treatment may be carried out on a system of spheres, and the earliest possible gel-point calculated as a function of C_v for a model which may be a fair approximation of reality. In this model it will be assumed that (1) all swollen polymer molecules are spheres of the same size. Actually, there will be a distribution of both size and shape, resulting in the calculation of too large a value of C_v at the gel-point. (2) After cross-linking, the spheres retain their shape. Actually, they would be expected to coalesce to some extent, but the resulting change in the value of C_v should be small. (3) Cyclic structures of spheres will be neglected. As cyclic structures reduce the effectiveness of cross-linking, the error introduced will lead to too small a calculated value of C_v at the gel-point and to some extent compensate the error introduced by assumption (1).

In order to treat this model, it is necessary to know the distribution of linkages between spheres. In the case that all spheres are mutually penetrable, the probability that a sphere possesses an additional linkage is probably independent of the number it already possesses. Accordingly, selecting the spheres as elements, the expected number of additional linkages possessed by a sphere already known to be singly connected is simply $\overline{N}$, the average number of linkages possessed by any sphere.[19] Actually the spheres are probably only slightly mutually penetrable, with the result that the distribution of linkages lies between complete randomness and the case where every sphere possesses exactly $\overline{N}$ linkages. In the latter case, the expected number of additional linkages possessed by a singly connected sphere is $\overline{N} - 1$, and we may locate the gel-condition as

$$1 < \overline{N} < 2 \qquad (5)$$

It is now merely necessary to obtain $\overline{N}$ in terms of C_v.

In the model under consideration, if a new sphere may be generated in the space inside a swollen sphere as well as outside, the average number of links formed by such a new sphere is given by $8C_v$.[20] The total number formed after n polymer molecules have been generated is

$$8 \int_0^n C_v \mathrm{d}n \qquad (6)$$

As every link is shared by two polymer spheres,

changing variables from n to c, the concentration of polymer molecules, gives

$$\overline{N} = \frac{16 \int_0^c C_v \mathrm{d}c}{c} \qquad (7)$$

The relation between c and C_v for a number of polymers has been found by Eilers[14] to be given by

$$c = \frac{C_v}{\dfrac{s_0 (s_0 - 1)C_v}{k}} \qquad (8)$$

where s_0 is the swelling factor at infinite dilution, and k a constant with a value between 0.74 and 1.00. Substituting (8) into (7) and integrating gives, if s_0 is large so that $s_0 - 1$ approximates s_0

$$\overline{N} = 16k \left[\left(\frac{k}{C_v} - 1 \right) \ln \left(1 - \frac{C_v}{k} \right) + 1 \right] \qquad (9)$$

Graphical solution of (9) for the cases of $\overline{N} = 1$ and $\overline{N} = 2$ gives $C_v = 0.13$ and $C_v = 0.23$, respectively, for both $k = 0.74$ and $k = 1.00$. Accordingly, the calculated value of the lowest value of C_v at which gelation can occur lies between 13 and 23%, in fair agreement, considering the assumptions employed, with the experimental values of $C_v = 25$–46%.

The foregoing discussion, it should be noted, is intended primarily to account for gelation at low extents of reaction. As the concentration of polymer in a system increases, interpenetration and entanglement of molecules becomes more important, and finally, as evidenced by the experiments in Table I containing 0.2 and 0.05% bifunctional monomer, a condition of homogeneity is achieved where gelation is quite accurately predicted by Equation (3).

Acknowledgment.—The writer wishes to thank Dr. F. R. Mayo for much helpful criticism and advice in the preparation of this paper, and Drs. R. H. Ewart and H. C. Tingey for numerous discussions of the properties of dilute polymer solutions.

Summary

1. Following Flory's method, an equation has been developed predicting the gel-point in the addition polymerization of a mixture of mono- and bifunctional monomers. This equation is shown to be equivalent to that developed by Stockmayer.

2. Gel-points for the systems methyl methacrylate–ethylene dimethacrylate and vinyl acetate–divinyl adipate have been determined under a variety of experimental conditions. Results are in reasonable agreement with the above equation only in the presence of 0.2 mole % or less of bifunctional monomer.

3. Experimental results in the presence of more bifunctional monomer are explained qualitatively on the basis that the reaction mixture consists of discrete swollen polymer molecules, the rate of

(19) This case is identical with the case of cross-linking of chains of equal length, the theory of which has been developed in detail by Flory, THIS JOURNAL, **63**, 3096 (1941).

(20) This may be shown as follows. Let there be m spheres of radius r in a volume V, and let a new sphere be generated. It will touch any sphere with a center within a distance of $2r$ from its center; i. e., within a volume $4/3 \ \pi(2r)^3$. If n is the total number of spheres, the average number of spheres with centers within this volume is $n \ 4/3\pi(2r)^3/V$, or since $C_v = n \ 4/3\pi r^3/V$, $8C_v$. This proof is independent of the degree of mutual penetrability of spheres, except for the assumption that a new sphere may be generated within an old one. If it cannot, a similar derivation yields $7C_v$.

diffusion of which is slow compared with the rate of polymer chain growth.

4. Employing a model based on this concept, it is calculated that gelation can only occur after these swollen molecules have filled 13–23% of the reaction mixture. Experimental results indicate 25–46% in fair agreement with calculation.

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The Acidic Constituents of Degras. A New Method of Structure Elucidation[1]

BY A. W. WEITKAMP

Introduction

Because of the unique complexity of degras (wool fat, wool wax) the identities of the individual acidic constituents have remained obscure. Early investigators[2,3,4] recognized the presence of two types of acids: (a) hydroxy acids ($C_nH_{2n}O_3$) and (b) acids of normal oxygen content ($C_nH_{2n}O_2$). Attempts to resolve the mixture by ester distillation were unsuccessful. Kuwata[5] obtained about 7% of impure $C_{16}H_{32}O_3$ by selective extraction with 90% methanol, followed by fractional distillation of the methyl esters of the extract. This acid was shown to be a "stereoisomer of synthetic α-hydroxyhexadecanoic acid." The structures of the acids of normal oxygen content have been variously postulated as normal,[6,7,8,9] branched[3,4,10,11] or even cyclic,[10] but there is no evidence that any such acids were isolated or identified.

The ester distillation method seemed to us to offer greater possibilities than solvent extraction as a means of separating the individual constituents, particularly since recent advances in column packings[12,13] have made possible the construction of highly efficient laboratory stills. The greatest deficiency of the ester distillation method as applied to this problem is that the methyl esters of the hydroxy acids are thermally unstable. Members of the 2-hydroxy series above $C_{16}H_{32}O_3$ have not been recovered.

The laboratory vacuum still used in this investigation was identical with one described in an earlier paper[14] except for the substitution of a more efficient, spiral-conical-pattern, 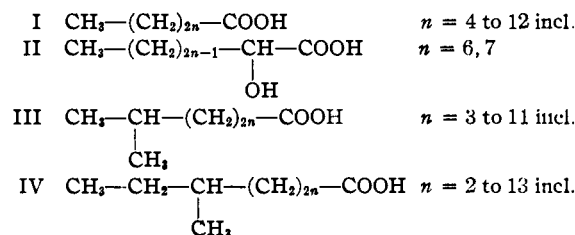wire gauze packing.[15] The packed section was 44 inches in length by one inch inside diameter. The over-all efficiency was approximately 100 theoretical plates.

The specimen of degras used in this study was taken from a commercial lot purchased in 1941 from Arlington Mills, 80 Chauncy St., Boston, Mass., under the brand name, "Centrifuged Degras." Its composition was as follows:

COMPOSITION OF DEGRAS, WT. %

Moisture	1.2
Free acids	11.0
Combined acids	44.0
Unsaponifiable (sterols, etc.)	46.1

The work reported in this paper was restricted to those acids originally present as sterol esters because of the possibility that the free acids might include extraneous acidic material, originating from the detergents used for scouring the wool. Altogether 32 acidic constituents have been isolated. These are distributed among four homologous series: (I) normal fatty acids, (II) optically active 2-hydroxy acids, (III) iso acids (methyl side chain in the penultimate position) and (IV) dextrorotatory anteiso[16] acids (methyl side chain in the antepenultimate position).

I $CH_3—(CH_2)_{2n}—COOH$ $n = 4$ to 12 incl.

II $CH_3—(CH_2)_{2n-1}—CH—COOH$ $n = 6,7$
$\qquad\qquad\qquad\qquad\quad |$
$\qquad\qquad\qquad\qquad\ OH$

III $CH_3—CH—(CH_2)_{2n}—COOH$ $n = 3$ to 11 incl.
$\qquad\quad\ |$
$\qquad\ CH_3$

IV $CH_3—CH_2—CH—(CH_2)_{2n}—COOH$ $n = 2$ to 13 incl.
$\qquad\qquad\qquad |$
$\qquad\qquad\ CH_3$

Isolation of Constituents

The free acids (110 g.) were extracted with alkaline 60% ethanol from a petroleum ether solution of degras (1000 g.). The sterol esters (878 g.) were saponified with potassium hydroxide and separated with petroleum ether and 60% ethanol into sterols (461 g.) and acids (440 g.). These acids were esterified with methanol and dry hydrogen chloride and finally filtered in petroleum ether solution through Attapulgus clay. The yield of neutral, straw-colored esters was 405 g. or 88% of the theoretical based on an average

(1) Presented before the Division of Organic Chemistry, New York meeting of the American Chemical Society, September 14, 1944.

(2) Chevreul, Compt. rend., 42, 130 (1856).

(3) Lewkowitsch, J. Soc. Chem. Ind., 11, 136 (1892); 15, 14 (1896).

(4) Darmstaeder and Lifschutz, Ber., 28, 3133 (1895); 29, 618, 1474, 2890 (1896); 31, 97, 1122 (1898).

(5) Kuwata, THIS JOURNAL, 60, 559 (1938).

(6) Busine, Wagners Jahresber., 30, 1189 (1884).

(7) Herbig, J. Soc. Chem. Ind., 15, 138 (1896).

(8) Rohmann, Biochem. Z., 77, 298 (1916).

(9) Drummond and Baker, J. Soc. Chem. Ind., 48, 232T (1929).

(10) Abraham and Hilditch, ibid., 54, 398T (1935).

(11) Kuwata and Ishii, J. Soc. Chem. Ind. Japan, 39, 317B, 318B, 358B (1936).

(12) Bragg, Ind. Eng. Chem., Anal. Ed., 11, 283 (1939).

(13) Lecky and Ewell, ibid., 12, 544 (1940).

(14) Weitkamp and Brunstrum, Oil & Soap, 18, 47 (1941).

(15) Weitkamp and Oblad (to Standard Oil Co. (Ind.)), U. S. Patent 2,325,818.

(16) Apparently there has been no name comparable to iso applied to the series of compounds having a methyl group at the third carbon atom. To fill this need the term, anteiso, was coined.