lected. In this connection, it is well to point out two things. First, the contribution of the I-disks to the length of the muscle fiber would not change the general shape of the stress–strain curve of muscle and, accordingly, would not destroy the close analogy of this curve to that of rubber and second, if the I-disks were considered, the extension for a given tension would become greater. This would decrease the calculated modulus of elasticity.

According to statistical theory the modulus of elasticity of randomly kinked molecular chains at zero extension is $3RTW/M$ where R is the gas constant, T is the absolute temperature, W is the weight of the elastic material per cubic centimeter, and M is the molecular weight of each chain. Kuhn[6] has considered the case of randomly oriented rigid rods connected end to end by flexible links and imbedded in an isotropic fluid matrix. The modulus of elasticity at zero extension which he obtained for such a system is $9RTW/5M$.

It is generally agreed that the protein, myosin, is responsible for the active elastic properties of muscle. It has been established that the only part of the muscle which contracts is made up of the so-called A-disks, and accordingly, it is probable that myosin is confined to the A-disks of the muscle. Myosin makes up about 10% of the total muscle[7] and A-disks occupy about half of the muscle. This means that about 20% of the A-disks is myosin or W is about 0.2. Ramsey and Street worked at 284° and R is 8.37×10^7 ergs per degree per mole. Then for randomly kinked flexible chains the molecular weight of each chain is about 40,000 and for randomly arranged rigid rods the molecular weight of each rod is about 24,000.

Only one of the several experiments of Ramsey and Street has been used. The choice of this experiment was solely a matter of convenience; it was easier to extrapolate to zero extension. It should be emphasized, however, that all the experiments of Ramsey and Street show the same type of stress–strain curve. Indeed, Ramsey and Street comment rather extensively on the "knee" (portion of the curve from the origin to A) shown in Fig. 1. They call this portion of the curve the delta region. A characteristic feature of a muscle which has once entered this region is that it will not spontaneously return to its initial resting length. In terms of the picture presented in this paper, the myosin has become so randomly arranged that it is no longer possible for it to recrystallize. Also characteristic of the Ramsey–Street experiments is the steep upswing of the stress–strain curve at lengths greater than the δ region. As we have pointed out above, this closely parallels the behavior of rubber and it is generally considered that this portion of the curve reflects a crystallization of the polymer. That this is a valid interpretation for muscle is indicated by the recent experiments of Fischer[8] who was able to show that for muscle undergoing contraction, the birefringence rose rapidly as the length of the contracted muscle approached that of the resting state.

According to the kinetic theory of muscle contraction outlined above, the contraction of a muscle should involve the absorption of heat. Actually, experiments indicate that heat is liberated when a muscle contracts.[9] This problem is not a simple one and cannot be gone into here. It is probable, however, that the complexity of the chemical reactions which proceed, accompany and follow muscle contraction is such that no safe conclusions can be drawn regarding the elastic nature of muscle from heat change studies. Many of the chemical reactions may be exothermic and completely obscure the heat absorption involved in the actual motion of the elastic element of muscle.

This theory also demands that the tension exerted by a muscle should increase with increasing temperature. Ramsey has kindly placed at my disposal 27 unpublished experiments in which he varied the temperature over the range from 2.4 to 22.6° Due to the extreme difficulty of this technique, there is considerable variability. These data have, however, been reduced to a common axis and the best straight line through the points calculated by the method of least squares. From this calculation, it was found that the factor of proportionality between the isometric tension and the absolute temperature at the resting length of the muscle fiber is 8.4×10^{-3} with a probable error of the mean of 3.6×10^{-3}. If the tension were directly proportional to the absolute temperature, the factor of proportionality would be 3.7×10^{-3}. These data certainly do not prove that the contraction of a muscle is rubber-like in nature, but they are in keeping with such an interpretation.

The problems outlined in this note have been discussed with a number of people and I am grateful to all of them for their comments. I wish especially to thank Dr. Robert W. Ramsey for sending me the detailed data for his tension-length experiments and for his kind permission to use some of his unpublished data.

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RECEIVED[10] AUGUST 24, 1945

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[6] Kuhn, *Kolloid-Z.*, **87**, 3 (1939).

[7] Edsall, personal communication.

[8] Fischer, *J. Cellular Comp. Physiol.*, **23**, 113 (1944).

[9] Brown, "Muscle," in Fenn, "Biol. Symp.," **3**, 161 (1941), The Jaques Cattell Press, Lancaster, Pa.

[10] Original manuscript received January 8, 1945.

Tensile Strength in Relation to Molecular Weight of High Polymers

BY PAUL J. FLORY

Sookne and Harris[1] have shown recently that the tensile strength of cellulose acetate depends

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[1] A. M. Sookne and M. Harris, *Ind. Eng. Chem.*, **37**, 478 (1945); *J. Research Natl. Bur. Standards*, **30**, 1 (1943).

explicitly on the *number average* molecular weight regardless of the molecular weight distribution. They have found also that the tensile strength (and other mechanical properties as well) of a "blend" composed of a mixture of cellulose acetate fractions equals the *weight average* of the tensile strengths of the components, *i. e.*

$$T_m = \sum_i w_i T_i \tag{1}$$

where w_i is the weight fraction of the component which by itself exhibits a tensile strength T_i and T_m is the tensile strength of the mixture. These seemingly incongruous statements can be reconciled only if the tensile strength–molecular weight relationship assumes a particular form, as will be shown below. In other words, these statements actually define the form of the relationship of tensile strength to molecular weight. This same relationship also applies to butyl rubber vulcanizates, and, hence, may be quite general.

Let the tensile strength be expressed as a function of $1/M$. Then

$$T = f(1/M) = a_0 + a_1/M + a_2/M^2 + \dots \tag{2}$$

where a_0, a_1, etc., are numerical coefficients in the series expansion of $f(1/M)$. According to the first stated characteristic of this function, the tensile strength of a mixture of cellulose acetate molecules differing in size is given by

$$T_m = f(1/\overline{M}_n) \tag{3}$$

where $\overline{M}_n$ is the number average molecular weight for the mixture. By definition

$$1/\overline{M}_n = \sum_i (w_i/M_i)$$

where M_i is the molecular weight of the i-th species. Hence

$$T_m = f(\sum_i w_i/M_i)$$

Employing the series expansion of Equation (2)

$$T_m = a_0 + a_1\sum_i(w_i/M_i) + a_2(\sum_i(w_i/M_i))^2 + \dots \tag{4}$$

Additivity of tensile strength according to the weight fractions of the components, as expressed by equation (1), requires that

$$\begin{aligned} T_m &= \Sigma w_i f(1/M_i) \\ &= a_0 + a_1\sum_i(w_i/M_i) + a_2\Sigma(w_i/M_i^2) + \dots \end{aligned} \tag{5}$$

The first two terms of equations (4) and (5) are identical, but higher terms differ. Consequently, the two characteristics of the dependence of tensile strength on molecular weight of cellulose acetate observed by Sookne and Harris are consistent only when a_2 and higher coefficients in equation (2) are equal to zero. The relationship then assumes the simple form

$$T = a_0 + a_1/M \tag{6}$$

in which M is to be replaced by the number average $\overline{M}_n$ when dealing with heterogeneous polymers. The same analysis can be applied to other properties which likewise seem to depend on the number average molecular weight and to exhibit additivity in their weight fractions.[1]

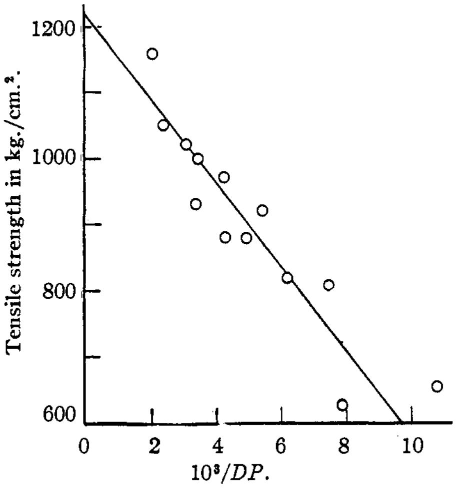

Fig. 1.—Tensile strength *vs.* reciprocal of chain length for cellulose acetate fractions. The data are those of Sookne and Harris (ref. 1).

In the accompanying figure Sookne and Harris' tensile strength values for fractions are plotted against the reciprocals of their degrees of polymerization determined by the osmotic pressure method. The relationship is linear within experimental error in agreement with equation (6), as necessarily must be the case in view of their observations stated in the first paragraph above. A similar dependence of tensile strength on molecular weight (before vulcanization) has been observed for butyl rubber vulcanizates[2] when the concentration of cross-linkages is held constant.

It is rather surprising that this similarity exists between two materials so fundamentally different in properties and structure. Vulcanized butyl rubber possesses a network structure owing to the cross-linkages between occasional units of the primary polymer molecules (one cross-linked unit for each 300 or more units); there are no cross-linkages in cellulose acetate. The latter is normally crystalline and elongates only some 25% at break; the former stretches to ten or more times its initial length and crystallizes only when stretched. The only evident features in common are their predominantly linear polymeric structures and the occurrence in each of them of high degrees of crystallinity when subjected to severe tension.

The dependence of the tensile strength of butyl rubber on its structure can be stated more generally: the tensile strength appears to be a *linear function of the percentage of the structure permanently oriented by stretching* over a wide range of structural variations. Within the network structure only "chains" (portions of the rubber molecules) extending from one cross-linkage to another are permanently oriented by stretching; chains

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(2) P. J. Flory, forthcoming publication.

reaching from the end of a primary molecule to the first cross-linkage along its length are not permanently distorted by a deformation of the sample. The latter, therefore, generally will not undergo crystallization, but rather will act like diluents dispersed in the oriented portion of the network

Equation (6) can be deduced as a special case of the more general dependence stated in *italics* above. If the concentration of cross-linkages (degree of vulcanization) is fixed, the percentage of the rubber occurring in non-orienting terminal chains will be inversely proportional to M, the molecular weight of the primary molecules (*i. e.*, the molecular weight of the rubber molecules before vulcanization). Hence, in accordance with the above generalization, the tensile strength varies linearly with $1/M$ at constant degree of cross-linking.

This interpretation of the tensile strength–molecular weight relationship cannot be applied to cellulose acetate which has no primary valence network. It would appear that the similar dependence on molecular weight in this case is to be regarded as coincidental rather than as an indication of identical structural behavior when subjected to severe stresses. In this connection Spurlin[3] has suggested that rupture originates at the ends of molecules and, hence, that the ease of failure (conversely the strength) should depend on the *number* of ends of molecules. This will explain the explicit dependence of strength on the number average molecular weight; it does not seem to offer a satisfactory basis for *linear* dependence on $1/M$, or $1/\overline{M}_n$, however.

[3] H. M. Spurlin, "Cellulose and Cellulose Derivatives," edited by Emil Ott, Interscience Publishers, Inc., New York, N. Y., 1943, pp. 9, 935–936.

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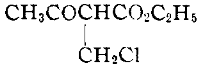
RECEIVED AUGUST 28, 1945

Reaction of Chloromethyl Ether with Ethyl Acetoacetate in the Presence of Boron Trifluoride[1]

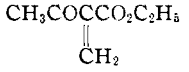
BY ROBERT LEVINE AND CHARLES R. HAUSER

It has been shown in this Laboratory[2] that, in the presence of boron trifluoride, certain ethers and alcohols alkylate acetoacetic ester to form the corresponding C-alkyl derivative. It has now been found that, under similar conditions, chloromethyl ether reacts with acetoacetic ester to form methylenediacetoacetic ester (III). The reaction involves presumably the chloromethylation of acetoacetic ester to form the C-alkyl derivative (I). This intermediate then either alkylates unchanged acetoacetic ester to form (III) or loses hydrogen chloride to form (II) which undergoes a Michael condensation with unchanged acetoacetic ester to form (III).



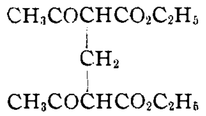
$$\begin{array}{l}\mathrm{CH_3COCHCO_2C_2H_5}\\ \qquad\ |\\ \qquad\mathrm{CH_2Cl}\end{array}$$

I



$$\begin{array}{l}\mathrm{CH_3COCCO_2C_2H_5}\\ \qquad\ \|\\ \qquad\mathrm{CH_2}\end{array}$$

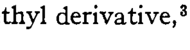
II



$$\begin{array}{l}\mathrm{CH_3COCHCO_2C_2H_5}\\ \qquad\ |\\ \qquad\mathrm{CH_2}\\ \qquad\ |\\ \mathrm{CH_3COCHCO_2C_2H_5}\end{array}$$

III

The chloromethylation with boron trifluoride to form the C-alkyl derivative is in contrast to the reaction of chloromethyl ether with sodium acetoacetic ester which forms mainly the O-methoxymethyl derivative,[3] $\mathrm{CH_3C{=}CHCO_2C_2H_5}$.



$$\begin{array}{l}\mathrm{CH_3C{=}CHCO_2C_2H_5}\\ \quad\ |\\ \quad\mathrm{OCH_2OCH_3}\end{array}$$

Procedure.—A mixture of one or one-half mole of chloromethyl ether and one-half mole of ethyl acetoacetate was saturated with boron trifluoride at 0° as described previously[2] for alkylation with ordinary alcohols and ethers. After the reaction mixture had come to room temperature, it was poured into aqueous sodium acetate. The mixture was extracted with ether and the dried ethereal extract distilled. There was obtained a 33% yield of methylene-diacetoacetic ester, b. p. 192–210° at 20 mm. with decomposition,[4] giving, with ferric chloride solution, a deep purple enol test, and with alcoholic ammonia, ethyl dihydrolutidinedicarboxylate, m. p. 174–176°.[4] A non-distillable viscous residue (10–13 g.) remained in the distilling flask.

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[1] Paper XXXI on "Condensations"; paper XXX, THIS JOURNAL, **67**, 1510 (1945).

[2] Adams, Abramovitch and Hauser, *ibid.*, **65**, 552 (1943).

[3] Simonsen and Storey, *J. Chem. Soc.*, **95**, 2108 (1909).

[4] Knoevenagel, *Ann.*, **281**, 94 (1894).

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RECEIVED SEPTEMBER 17, 1945

Determination of Pyrrole

BY F. FROMM[1]

A photometric micromethod for the determination of pyrrole has been based on the blue color produced in the reaction between pyrrole and isa-

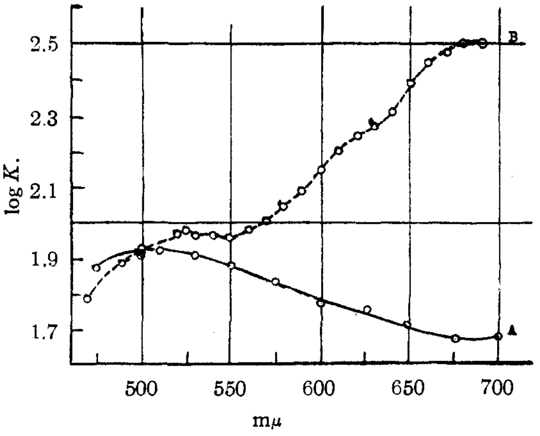

Fig. 1.—A, color reaction; 10.8 mg. pyrrole per liter: B, pyrrole blue B; 5.3 mg. pyrrole per liter.