Die Deutung dieser abwechselnden Kontraktion und Streckung des Fadens kommt nach dem eingangs Gesagten dadurch zustande, daß bei Zusatz von Alkali infolge gegenseitiger Abstoßung der auf dem Faden befindlichen COO^--Ionen eine teilweise Entknäuelung und damit eine Streckung der zwischen Verknüpfungspunkten des Netzwerkes liegenden Fadenteile (der Netzbögen) herbeigeführt wird. Bei Säurezusatz findet ein Übergang der COO^--Ionen in nichtgeladene COOH-Gruppen statt; die teilweise entknäuelten Netzbogen haben das Bestreben, in die wahrscheinlichste Konstellation zurückzukehren; sie bewirken dadurch eine Kontraktionstendenz in ähnlicher Weise, wie dies beim gedehnten Kautschuk der Fall ist.

Nach einer brieflichen Mitteilung von A. KATCHALSKY hat er zusammen mit H. VOGEL ein Kopolymerisat von Methacrylsäure und Divinylbenzol hergestellt, welches bei abwechselndem Zusatz von Alkali und Säure sehr stark quillt und entquillt. (Siehe die nachfolgende Mitteilung von A. KATCHALSKY). Es handelt sich um Beobachtungen, welche zu unsern Versuchen weitgehend analog sind, mit dem Unterschied, daß die Orientierung der Netzbögen bei diesen isotropen Präparaten fehlt.

Mit Sicherheit ist gezeigt, daß die Formänderung, welche bei Ladungsänderungen polyvalenter Fadenmoleküle eintritt, vom gelösten Einzelfaden auf makroskopische Systeme überführt und zur Leistung mechanischer Arbeit verwendet werden kann.

Ursprung der freien Energie für die Arbeitsleistung bei der Kontraktion: wenn wir, was sich mit unserem Faden durchführen läßt, den unbelasteten Faden durch Zusatz von Alkali dehnen, ihn dann belasten und den belasteten Faden durch Zusatz von Säure zur Kontraktion bringen, so ist chemische Energie in mechanische Energie umgesetzt worden. Diese rührt davon her, daß die Netzbögen beim belasteten Faden stärker entknäuelt sind als bei gleichem p_H oder gleichem Ionisationsgrade beim unbelasteten Faden. Nun ist beim künstlich entknäuelt gehaltenen Faden die effektive Säuredissoziationskonstante der COOH-Gruppen größer als beim sonst gleichen, stärker geknäuelten Faden. Die freie Energie, welche bei der Freisetzung der Polyacrylsäure bei Zusatz von HCl zum Na-Salz auftritt, ist also beim belasteten und unbelasteten Faden ungleich groß und es ist diese Differenz, welche als mechanische Arbeitsleistung in den beschriebenen Versuchen auftritt.

W. KUHN

Physikalisch-Chemisches Institut der Universität Basel, den 20. Mai 1949.

Summary

A three-dimensional network containing oriented filaments of polyacrylic acid can be obtained by heating mechanically stressed foils of this substance, containing some glycerol and some sulfuric acid.

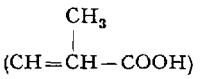
Those filaments, if suspended in water, swell anisotropically. They contract and dilate reversibly upon alternating addition of small amounts of acid and alkali to the medium in which they are suspended.

Rapid Swelling and Deswelling of Reversible Gels of Polymeric Acids by Ionization

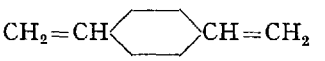
(A synthetic "Contractile System")

As a result of the investigation of aqueous solutions of polymeric acids[1] it was suggested that the change of the properties of the solutions with ionization is due to a corresponding change in the molecular shape. It was assumed that with increasing p_H, i.e. increase in the degree of ionization, the polymer molecules are stretched by the electrostatic repulsive forces acting between the carboxylate ions; conversely, upon neutralization of the charged groups the molecule is again coiled by the Brownian movement. This hypothesis was successfully applied to the interpretation of the viscosity, double refraction of flow, and potentiometric titration of solutions of polymeric acids.

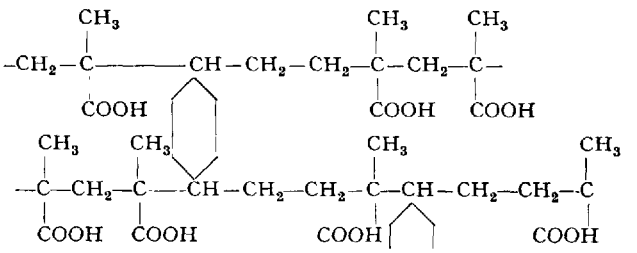
It was felt, however, that the changes brought about by the charging of the molecules might also occur on a macroscopic scale in systems exhibiting contractions and dilatations, such as biological systems of the muscle type. A model system of this type was obtained by copolymerizing methacrylic acid



with a low percentage of divinyl benzene



to give a three dimensional, cross-linked polymer, of the general formula:—



This copolymer swells to a remarkable extent in aqueous alkali. A small sample of the substance may be induced to perform many rapid and reversible contractions and dilatations under the microscope by successive additions of acid and alkali. Intermittent washing with distilled water is necessary to remove the salt formed in the process of neutralization.

In order to get a quantitative measure of the degree of swelling under the influence of alkali the following experiments were performed:— Small amounts of copolymer were soaked in water containing sufficient alkali to neutralize a definite fraction (α) of the carboxylic groups. During a few hours practically all the alkali was taken up and the polymer swollen to a considerable extent (thermodynamic equilibrium is attained only after a longer time). The weight ratio (W) of the swollen polymer to the original increases steadily with α to a maximum value and then at very high degrees of

[1] A. KATCHALSKY and P. SPITNIK, J. Polym. Sci. *2*, 432 (1947). – W. KUHN, O. KUENZLE, and A. KATCHALSKY, Bull. Soc. Chim. Belg. *57*, 421 (1948); Helv. chim. acta *31*, 1994 (1948); J. Polym. Sci. in the press.

ionization begins to decrease slowly (Fig. 1). The degree of swelling, compared with other equilibrium type gels, is very large. On adding mineral acid the highly swollen gels contract rapidly to the original volume.

These phenomena may be interpreted as follows:—The equilibrium swelling of the polymeric acid gels is brought about by two opposing tendencies:—

(1) The solution tendency of the polymeric molecules and the osmotic pressure of the cations of the alkali bound by the gel.

(2) The caoutchouc-type contraction tendency of the stretched polymer molecules.

As in our case the polymeric acid is ionized and stretched by the electrostatic repulsion of the carboxylate ions, this contraction tendency is diminished to a considerable extent, and the gel can be swollen with greater ease than non-charged molecules. As soon as the ionized groups are neutralized by the addition of strong acid, the polymer molecules begin to contract and press out the imbibed water. At high degrees of neutralization the concentration of the opposing ions in the gel becomes large enought to screen the negative charges and thus diminishes the electrostatic repulsion of the carboxylate ions; thus, at neutralization degrees higher than 70% further addition of alkali causes contraction of the gel. Similar phenomena were observed in the viscosity of solutions of polymethacrylic acid.

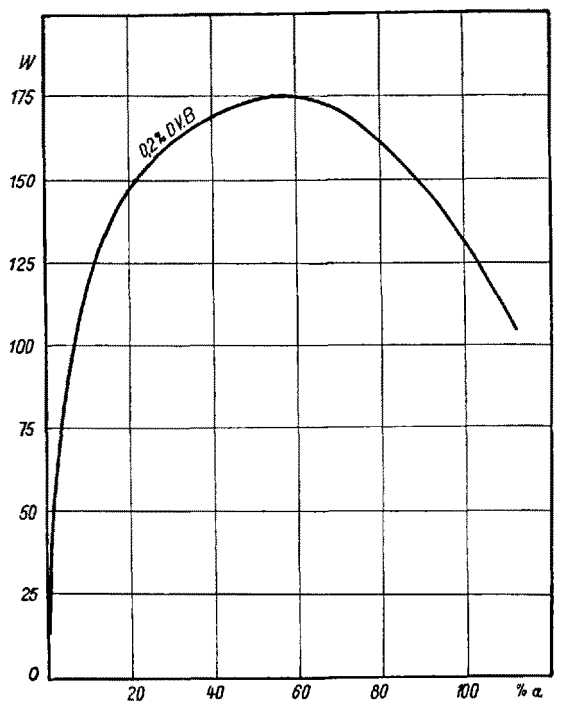


Fig. 1. – Equilibrium swelling of a methacrylic acid-divinyl benzene copolymer (0·2% D.V.B.) in aqueous alkali.
W The weight ratio of the swollen to the unswollen polymer.
α The percentage of neutralization of the carboxylic groups.

As might be expected, the swelling capacity decreases with increasing degree of cross-linking. In Fig. 2 are given the results of a series of experiments with copolymers of different divinyl benzene content.

In the phenomena discussed here the chemical ionization energy is transformed directly into mechanical energy. We may therefore regard them as the first synthetic examples of mechanochemical systems. In subsequent papers similar models based upon polar derivatives of butadiene and exhibiting greater mechanical strength will be presented.

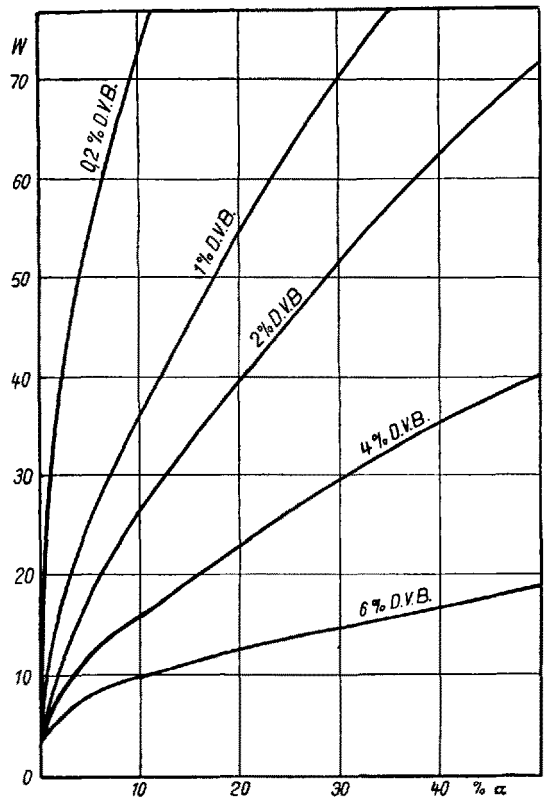


Fig. 2. – Equilibrium swelling of methacrylic acid divinyl benzene copolymers of different divinyl benzene (D.V.B.) content at various degrees of neutralization of the carboxyl groups with aqueous NaOH.
W The weight ratio of the swollen to the unswollen polymer.
α The percentage of neutralization of the carboxyl groups.

In the course of our work we learned from W. KUHN about his interesting experiments on anisotropic but very similar systems exhibiting a strong and rapid contractibility. As the theoretical framework of the behaviour of polymeric electrolytes was the result of a long-standing co-operation with W. KUHN and his school in Basle it was decided to publish this note simultaneously with his.

The author wishes to express his thanks to Miss H. VOGEL for help in carrying out the experiments.

AHARON KATCHALSKY

The Weizmann Institute of Science, Rehovoth, Israel, June 10, 1949.

Résumé

Le gonflement et dégonflement rapide et accentué des copolymers de l'acide méthacrylique et du divinyl benzène dans des solutions aqueuses alcalines et acides ont été étudiés.

Les phénomènes ressemblent aux contractions et dilatations des systèmes biologiques.

L'interprétation donnée est basée sur l'effet du redressement des chaînes moléculaires sous l'influence de la répulsion électrostatique des groupes carboxyliques ionisés, qui se contractent lors de la neutralisation des charges.