The Mechanical Behavior of Swollen Polymethyl Acrylate Gels.
II. The Stress Relaxation in Organic Solvents

By Kazuyoshi OGINO

(Received February 4, 1958)

In the previous paper¹⁾ the interaction parameter μ between polymer and solvent has been determined for slightly cross-linked polymethyl acrylate gels in equilibrium with several organic solvents, from their initial stress-strain relations. Although these gels respond purely elastically to a rapid deformation, it is observed that the stress relaxes with time under a constant deformation. The stress relaxation and its dependency upon the degree of swelling of these gels are investigated in the present paper.

The stress-strain behavior of a visco-elastic body may be expressed by the Maxwell equation, or by generalizing the Maxwell theory in consideration of a distribution of relaxation times.

If the distribution of relaxation times is continuous, the rate of strain, $\mathrm{d}s/\mathrm{d}t$, is expressed as,

$$\frac{\mathrm{d}s}{\mathrm{d}t}=\frac{1}{E(\tau)}\cdot\frac{\mathrm{d}f(\tau,t)}{\mathrm{d}t}+\frac{1}{\tau\cdot E(\tau)}\cdot f(\tau,t)$$

where $f(\tau,t)$ and $E(\tau)$ are the distribution functions of the stress and the elastic modulus respectively. Total stress is expressed as,

$$f(t)=\int_0^\infty f(\tau,t)\mathrm{d}\tau.$$

Then, at a constant strain s_0, the decay of stress with time can be expressed as follows:

$$\begin{aligned}f(t)&=\int_0^\infty s_0\cdot E(\tau)\cdot\exp\cdot(-t/\tau)\cdot\mathrm{d}\tau\\&=s_0E(t)\end{aligned}\qquad(1)$$

where $E(t)$ is the relaxation elastic modulus, which can be determined by the experiment. $E(\tau)$, which is the distribution function of elastic modulus, is a fundamental measure of the mechanical behavior of a substance. Several methods have been proposed to obtain this function approximately from the experimental curves²⁾.

As a first approximation we can replace the function $\exp.(-t/\tau)$ in equation 1 by step function $K(t,\tau)$, which is defined as follows:

$$K(\tau,t)=\begin{cases}1\ \cdots\cdots\ t<\tau\\0\ \cdots\cdots\ t>\tau\end{cases}$$

Then equation 1 turns out to be

$$E(t)=\int_t^\infty E(\tau)\cdot\mathrm{d}\tau$$

then,

$$E(\tau)=-\mathrm{d}E(t)/\mathrm{d}t$$

Using the latter relation, we can obtain the distribution function of elastic modulus among the various relaxation times experimentally from the negative slope of the observed relaxation curve.

On the other hand, Tobolsky et al. found that³⁾ the shape of the relaxation curve for a given polymer is the same at different temperatures, when plotted as reduced stress* against logarithmic time, but a change in temperature essentially shifts the position of the curve along the logarithmic time scale.

Experimental

Sample.—Cross-linked polymethyl acrylate used in this experiment is the same as described in the previous paper¹⁾. Samples are brought to the swelling equilibrium with chloroform, benzene, toluene, carbon tetrachloride and methanol.

Apparatus.—The specimen is vertically compressed to a given height, and the stress which corresponds to the strain is recorded continuously by means of a chainomatic balance (the same one as was used in the previous work¹⁾) which is equipped with an automatically balancing system. This is shown in Fig. 1. The apparatus is the same as originally used by Guth⁴⁾ for the measurement of stress relaxation of cork, and recently improved by Fujita et al.⁵⁾.

---

1) K. Ogino, This Bulletin, **31**, 577 (1958).

2) H. Fujita, *Busseiron Kenkyu*, **63**, 48 (1953), (*in Japanese*)

* The stress is arbitrarily reduced to 25°C. The reduced stress g_{25} is calculated by multiplying the actual experimental stress value, f, by $298/T$, where T is absolute temperature.

3) A. V. Tobolsky et al., *J. Polym. Sci.*, **3**, 669 (1948).

4) S. L. Dart and E. Guth, *J. Apply Phys.*, **17**, 314 (1946).

5) H. Fujita, K. Ninomiya and T. Homma, This Bulletin, **25**, 271 (1952).

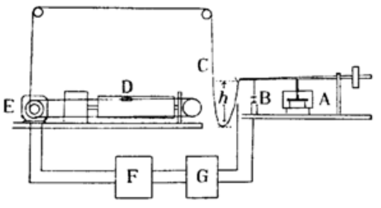

Fig. 1. The apparatus for the measurement of stress relaxation.
(A): Specimen (B): Contact
(C): Chain (D): Pencil for recording
(E): Balancing motor (F): Relay
(G): Amplifier circuit

In Fig. 1, (A) is the specimen at a given constant strain, and the stress is measured by the suspended length of a chain (C), which is controlled by the reversible motor (E) through the relay (F) and the amplifier circuit (G).

The reduced stress g_{25} at t°C can be expressed as follows

$$g_{25}=\frac{h\cdot d\cdot \boldsymbol{G}\cdot n}{A_0}\cdot\frac{298}{t+273}\ \text{dyne/cm}^2$$

where, h the vertical component of the chain length from the arm, d the linear density of the chain, n the magnification of the arm, that is the ratio of the distances to the hook and to the pressure plate from the fulcrum, A_0 the cross-sectional area of the sample, t the temperature of the sample, and $\boldsymbol{G}$ is the acceleration of gravity. In this apparatus, n is about 4.3. The experimental curves of reduced stress against logarithmic time scale obtained by this method are shown in Fig. 2.

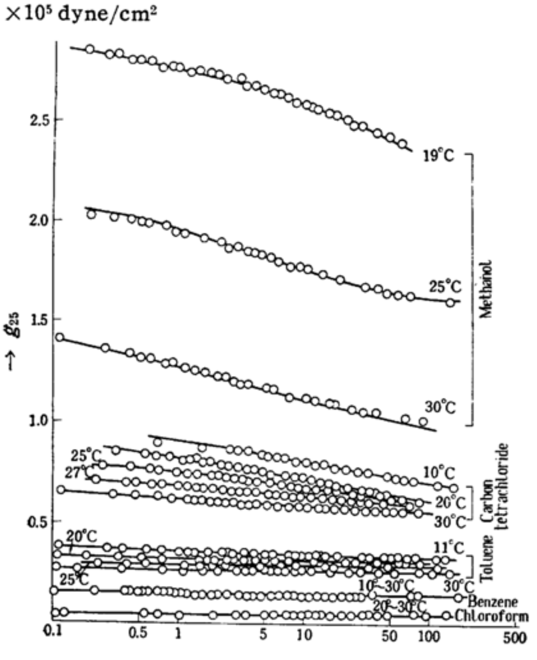

Fig. 2. The curves of reduced stress g_{25} against logarithmic time.

Results and Discussion

It is obvious from Fig. 2 that the smaller degree of swelling corresponds to the larger magnitude of stress, and to the larger degree of stress relaxation. For the good solvents, such as benzene or chloroform, relaxation curves at different temperatures expressed in reduced stress nearly overlap with each other. The slight dependency upon temperature means the small activation energy in relaxation.

Stress relaxation corresponds primarily to the breakage of some sort of linkage, such as secondary bonds or entanglement which are formed in the gel structures. As weak linkages may exist hardly at all in the well-swollen gels, only some strong linkages remain unbroken. As the weak linkages which are present at lower temperatures would be broken at higher temperatures, the degree of relaxation at higher temperatures is less remarkable than at lower temperatures. The greater temperature dependency, i. e., the greater activation energy, is expected for a poor solvent than for a good solvent. (Tobolsky has calculated this apparent activation energy for relaxation process[3,6]. But in this work, its calculation was not carried out, considering the large error involved in the data of the initial stress.) When the curves in Fig. 2 are superposed upon each other by sliding along the logarithmic time scale, master curves as shown in Fig. 3 are obtained. The slope of the master curve is large for the small degree of swelling, and for the high degree

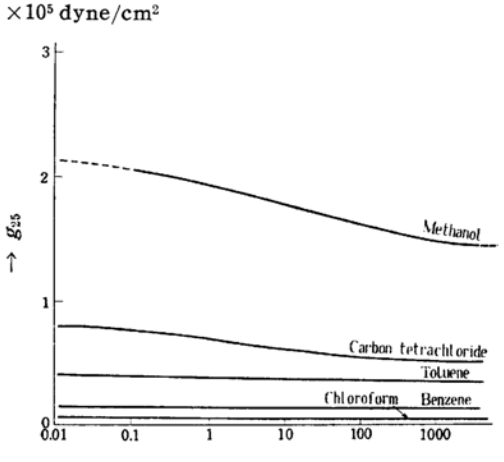

Fig. 3. The master curve of gels for each solvent.

---

[6] G. M. Brown and A. V. Tobolsky, *J Polym. Sci.*, **6**, 165 (1951).

of swelling, a constant slope over the wide range of the time scale is observed. This means that the height of distribution function $E(\tau)$ becomes higher, while its width is restricted, when the degree of swelling is small.

For the actual relaxation phenomena, the continuous distribution of relaxation times must be taken into account as mentioned above. However, how these phenomena can be expressed by the spring-dashpot model is now considered, applying the four-element system as shown in Fig. 4. To determine the magnitude of each parameter in this system, from actual relaxation data, the following method has been proposed⁷⁾.

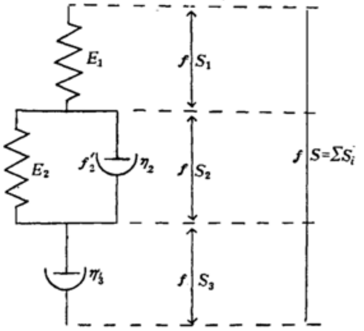

Fig. 4. The four-element model.

In the model shown in Fig. 4, the total strain $s=\sum_j s_j$, and f is the reactant stress.

Thus the following equations are obtained:

$$f/s_1=E_1$$
$$f_2/s_2=E_2 \;:\; f'_2/\dot{s}_2=\eta_2 \;:\; f_2+f'_2=f$$
$$f/\dot{s}_3=\eta_3$$

From these relations, we obtain at a constant strain,

$$\ddot{f}+\left\{E_1\left(\frac{1}{\eta_2}+\frac{1}{\eta_3}\right)+\frac{E_2}{\eta_2}\right\}\dot{f}+\frac{E_1E_2}{\eta_2\eta_3}\cdot f=0 \tag{1}$$

The solution of equation 1 can be expessed as follows

$$f=Ae^{-\alpha t}+Be^{-\beta t} \tag{2}$$

where,

$$\begin{cases} 2\alpha=\left[\dfrac{E_1}{\eta_3}+\dfrac{E_2}{\eta_2}+\dfrac{E_1}{\eta_2}\right] \\ \qquad -\sqrt{\left[\dfrac{E_1}{\eta_3}+\dfrac{E_2}{\eta_2}+\dfrac{E_1}{\eta_2}\right]^2-4\dfrac{E_1E_2}{\eta_2\eta_3}} \\ 2\beta=\left[\dfrac{E_1}{\eta_3}+\dfrac{E_2}{\eta_2}+\dfrac{E_1}{\eta_2}\right] \\ \qquad +\sqrt{\left[\dfrac{E_1}{\eta_3}+\dfrac{E_2}{\eta_2}+\dfrac{E_1}{\eta_2}\right]^2-4\dfrac{E_1E_1}{\eta_2\eta_3}} \end{cases} \tag{2'}$$

If a rapid strain $s=s_0$ was given at $t=0$, from equation 2,

$$\begin{cases} A=\dfrac{-\beta f_{t=0}-\dot{f}_{t=0}}{\alpha-\beta} \\ B=f_{t=0}-A \end{cases} \tag{3}$$

and,

$$\begin{cases} E_1\cdot s_0=f_{t=0} \\ \dfrac{\dot{f}_{t=0}}{E_1}=-\dfrac{f_{t=0}}{\eta_2}-\dfrac{f_{t=0}}{\eta_3} \text{ or } \dfrac{1}{\eta_2}+\dfrac{1}{\eta_3}=-\dfrac{s_0\cdot\dot{f}_{t=0}}{f^2{}_{t=0}} \end{cases} \tag{3'}$$

From these general relations, we can determine the values of four parameters.

For simplicity, we calculate for the case when $\alpha\ll\beta$. For the large value of $t=t_l$, we can neglect the second term in equation 2 and,

$$\alpha=-\dot{f}_{t=t_l}/f_{t=t_l} \tag{4}$$
$$A=\frac{f_{t=t_l}}{e^{(\dot{f}t=tl/ft=tl)\cdot t_l}} \tag{5}$$

From equation 3, 4 and 5, we obtain

$$B=f_{t=0}-\frac{f_{t=t_l}}{e^{(\dot{f}t=tl/ft=tl)\cdot t_l}} \tag{6}$$
$$\beta=(-\dot{f}_{t=0}-\alpha A)/B \tag{7}$$

and from equation 2′

$$\alpha+\beta=(E_1/\eta_3+E_2/\eta_2+E_1/\eta_2) \tag{8}$$
$$\alpha\beta=E_1E_2/\eta_2\eta_3 \tag{9}$$

From 4—7, we obtain α, β, A and B, and with these values, from 8 and 9, we obtain two equations for parameters. Combining these equations with equation 3′, we can calculate four parameters. These parameters at 25°C calculated by this method are listed in Table I.

These results show that at the small degree of swelling, or at the large value of v_r, the values of each parameter become larger. This is naturally expected from the fact that the small degree of swelling means the large concentration of the polymer substance in gel.

E_1 is the so-called instantaneous elasticity, and has a large value for the small degree of swelling. This may be due to the presence of many remaining secondary bonds besides the strong primary bonds for the small degree of swelling**. η_3 is the viscosity coefficient for the flow after the attainment of the stationary flow, and

---

7) T. Alffey, "Mechanical Behavior of High Polymers", Interscience Pub., Inc., N.Y. (1948) p. 181.

** From the theory of rubber elasticity, for instance, the stress is inversely proportional to the average molecular weight, M_c, between the junction points.

TABLE I
THE VALUS OF EACH PARAMETER FOR FOUR-ELEMENT MODEL

Solvent	Parameter						
	v_r	E_1 dyne/cm².	E_2 dyne/cm².	η_2 poise	η_3 poise	η_2/E_2 sec.	η_3/E_1 sec.
Methanol	0.68	0.98×10^6	5.2×10^6	1.5×10^9	9.6×10^{11}	3.0×10^2	1.0×10^6
Carbon tetrachloride	0.50	$3.9_7\times10^5$	8.4×10^5	2.9×10^8	1.1×10^{11}	3.5×10^2	2.6×10^5
Toluene	0.19	2.0×10^5	1.6×10^6	6.5×10^7	4.2×10^{10}	4.0×10^1	2.1×10^5
Chloroform	0.036	$3.4_5\times10^4$	5.1×10^5	2.3×10^7	$8.9_7\times10^9$	4.0×10^1	2.5×10^5

has also a large value for the small degree of swelling. Such a flow may have originated from the squeezing out of solvent which is contained between networks, or from the breaking of many junction points. These inferences are consistent with the order of the degree of swelling and the value of η_3. η_2 and E_2 characterize the part which expresses the transient state from instantaneous deformation to final steady flow, which occurs in a comparatively short time after the strain is imposed ($10^1\sim10^2$ sec., expected from η_2/E_2 in Table I), and may reflect the change of the inner structures. η_2 and E_2 have always larger values as the degree of swelling is lower. Taking account of the fact that η_2 and E_2 large, it seems that the weaker bond would be broken faster after the strain is imposed, or the solvent which can be pushed out more easily from the network would be squeezed out more readily.

In chloroform or benzene, polymer swells to a large extent, so that the greater part of the gel is occupied by solvent. The appearance of this gel is very soft. The mechanical behavior of these gels can be expressed by a simple Maxwell model as shown in Fig. 5 ($\ln f/f_0$ plotted against t). The slope of this curve gives $-1/\tau$, where τ is relaxation time. The relaxation time obtained from this method is approximately in agreement with the value η_3/E_1 of the four element model.

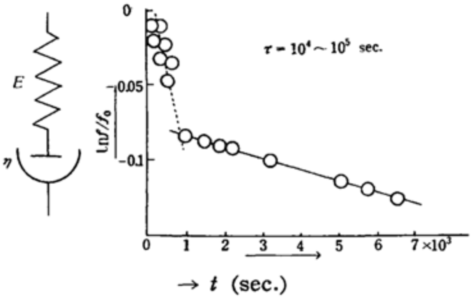

Fig 5. The curve plotted $\ln f/f_0$ against t for benzen.

Chain molecules in these gels are fixed at several junction points by cross-linking, and the interaction between these chains is considered to be stronger than in an ordinary polymer solution. The effect of this interaction appeared in the difference of dependency of stress relaxation upon the degree of swelling. The more detailed discussion must be expected from thermodynamic consideration of elasticity.

The author is particulary indebted to Professor H. Akamatu and Assistant Professor T. Nakagawa for their discussion and encouragement during this investigation, and to Mr. H. Arakawa, the University of Shizuoka, especially for his suggestion about the analysis by a four-element model.

Department of Chemistry, Faculty of
Science, The University of Tokyo
Hongo, Tokyo