The Mechanical Behavior of Swollen Polymethyl Acrylate Gels. I. The Determination of Polymer-Solvent Interaction Parameter μ by the Mechanical Measurement

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When a slightly cross-linked linear chain polymer is in contact with a solvent, it absorbs the solvent and expands to a limited volume, attaining the so-called swollen gel state. In this case, the interaction forces between the polymer and the solvent are considered to be one of the important factors which determine the degree of swelling of this system. A parameter which is called the polymer-solvent interaction patameter μ is employed to express the power of solvation. Mullin[1] showed that this parameter could be determined mechanically by the measurement of initial stress-strain relations using a gel of vulcanized natural rubber swollen in an organic solvent.

In this paper, the author determined this parameter μ of slightly cross-linked polymethyl acrylate gels swollen in several organic solvents, following the same method reported by Mullin.

Theory

The force f required to strain a gel to an extension ratio λ is given by[2]

$$f=2A_0(\lambda-\lambda^{-2})v_r^{-1/3}(\partial W/\partial I_1+\lambda^{-1}\partial W/\partial I_2) \tag{1}$$

where A_0 is the unstrained area of cross section, v_r the volume fraction of polymer at swelling equilibrium, W the free energy of deformation per unit volume, called as the stored energy function, and I_1 and I_2 are strain invariants which are defined as follows;

$$I_1=\lambda_1^2+\lambda_2^2+\lambda_3^2$$
$$I_2=\lambda_1^{-2}+\lambda_2^{-2}+\lambda_3^{-2}$$

where λ_1, λ_2 and λ_3 are the principal extension ratios.

This relation can also be expressed as follows[1]

$$f=2A_0(\lambda-\lambda^{-2})v_r^{-1/3}(C_1+\lambda^{-1}C_2) \tag{2}$$

In this relation, C_1 and C_2 are constants, and are obtained experimentally. Since the value of C_2 decreases to zero at a high degree of swelling ($v_r \leqq 0.25$), the equation 1 or 2 is reduced to the form predicted by the kinetic theory, if

$$C_1(\text{swollen})=\frac{1}{2}\cdot\rho\cdot\boldsymbol{R}\cdot\boldsymbol{T}\cdot M_c^{-1} \tag{3}$$

where ρ is the density of pure solvent, and M_c a parameter, which can be assumed as the average molecular weight between junction points.

On the other hand, at swelling equilibrium with solvent, the following equation is obtained from statistical consideration[3],

$$\ln(1-v_r)+v_r+\mu v_r^2=-\rho V_0 v_r^{1/3}/M_c \tag{4}$$

Or, from equation 3

$$-\ln(1-v_r)-v_r-\mu v_r^2=2V_0C_1v_r^{1/3}/\boldsymbol{RT} \tag{5}$$

In practice, the value of C_1 for a swollen gel can be obtained either by direct measurements of a high degree of swelling or by plotting the results of the simple extension measurement as

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[1] L. Mullin, *J. Polym. Sci.*, **19**, 225 (1956).

[2] S. M. Gumbrell, L. Mullin and R. S. Rivlin, *Trans. Faraday Soc.*, **49**, 1495 (1953).

[3] P. J. Flory and J. Rehner, *J. Chem. Phys.*, **11**, 512 (1943); M. L. Huggins, *J. Am. Chem. Soc.*, **64**, 1712 (1942).

$f\{2A_0(\lambda-\lambda^{-2})\}^{-1}v_r^{1/3}$ against λ^{-1} and extrapolating the curve to $\lambda^{-1}=0$.

With the value of C_1 thus obtained, the parameter μ can be determined by the equation 5.

Experimental

Sample — Commercial methyl acrylate was purified by shaking with aqueous alkaline solution, and was redistilled under reduced pressure. Diallyl adipate which was used as cross-linking agent was synthesized by esterification of allyl alcohol with adipic acid in the presence of *p*-toluene sulfonic acid as catalyst, and purified by fractional distillation under reduced pressure.

α-α'-azodi-*iso*-butyronitrile, used as initiator, was prepared according to Thiele and Heuser4), and was recrystalized from ether.

About 8 cc. of methyl acrylate monomer which contains one drop (about 3 mg.) of the cross-linking agent and about 30 mg. of the initiator was polymerized in bulk in a sealed glass tube. The polymer rod was then cut into several pieces, about 1 cm. in length, and immersed into the solvent to be tested.

Organic solvents used in this experiment are chloroform, benzene, toluene and carbon tetrachloride. They were purified in the usual way.

Apparatus.—The apparatus used in this experiment is shown in Fig. 15,6)*.

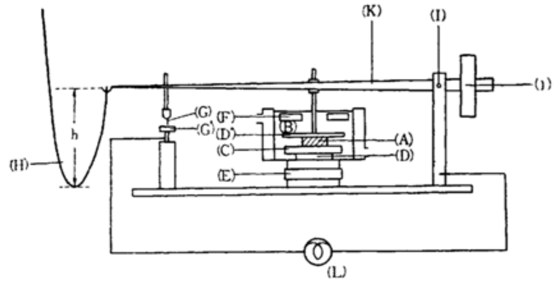

Fig. 1. The apparatus used in this experiment.
A: Specimen. B: Solvent. C: Iris of microscope. D: Brass block. D': Pressure plate. E: Screw gauge. F: Desiccating agent. G and G': Contacts. H: Chain. I: Fulcrum. J: Balancing weight. K: Beam.

Specimen A in the swelling equilibrium with a solvent B was placed between a flat brass block D and a pressure plate D', and was strained to a definite extent by rotating the screw E which was graduated to 0.01 mm., and the stress was measured by the chain H with the known linear density.

Force f in equation 2 at each strain can be calculated by the following equation

$$f=(bdhg)/a$$

where d is the linear density of the chain, h the vertical component of the chain length suspended from the beam, b the distance from the fulcrum to the chain, a the distance from the fulcrum to the center of the pressure plate and g the acceleration of gravity. In this experiment, $b/a\approx 4.3$, and d was 0.80 or 0.39 g/cm.

The temperature of the sample was controlled by circulation of water from a water bath kept at 25±0.5°C, and was read directly by a thermometer inserted in the solvent.

Results and Discussion

When W_b and W_a are the weights of the polymer before and after swelling, ρ_1 and ρ_2 are the densities of the solvent and of the polymer, respectively, the volume fraction v_r of the polymer after swelling can be given by the following equation7);

$$v_r=\frac{1}{1+\frac{\rho_2}{\rho_1}\left(\frac{W_a}{W_b}\right)-\frac{\rho_2}{\rho_1}}$$

The results are shown in Table I. The solvent, in which a gel has a small value

TABLE I
THE VALUES OF VOLUME FRACTION OF POLYMER, v_r, AND μ AT 25°C.

Solvent	v_r	$1/v_r$	$\mu_{25^\circ\mathrm{C}}$
Chloroform	0.035_5	28.2	0.49
Benzene	0.065_9	15.2	0.51
Toluene	0.192_5	5.2	0.54
Carbon Tetrachloride	0.501_0	2.0	0.69

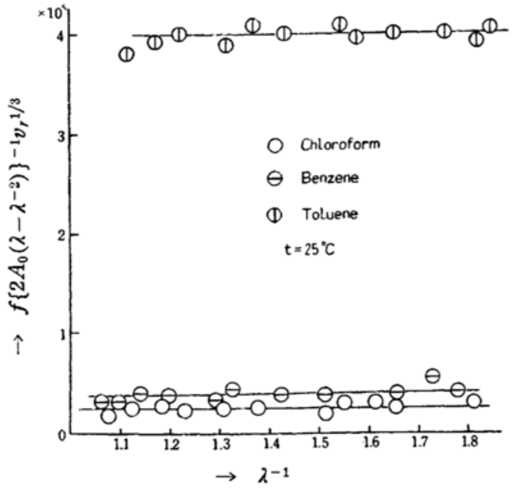

Fig. 2. The plot of $f\{2A_0(\lambda-\lambda^{-2})\}^{-1}v_r^{1/3}$ against λ^{-1} at 25°C.

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* This apparatus has been designed for the measurement of stress relaxation.

4) J. Thiele and K. Heuser, *Ann.*, **290** (1896).

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

6) H. Fujita, K, Ninomiya and T. Homma, This Bulletin, **25**, 374 (1952).

7) P. Doty and H. S. Zable, *J. Polym. Sci.*, **1**, 90 (1946).

of v_r, may be considered approximately to be a good solvent, because polymer-solvent contacts are attained sufficiently in it. From this table, we can assume that the solvent becomes poorer in the order of chloroform, benzene, toleuene and carbon tetrachloride.

An example for the plot of $f\{2A_0(\lambda-\lambda^{-2})\}^{-1}v_r^{1/3}$ against λ^{-1} is shown in Fig. 2. There is a good linear relationship between these two quantities. Extrapolation of the curve to $\lambda^{-1}=0$ gives C_1. The value of μ can be determined with the use of these values of C_1 and v_r. The results are shown in Table I. These values are about 0.50 except for carbon tetrachloride, and decrease in the order, toluene$>$benzene$>$chloroform. We can say that chloroform is the best solvent for polymethyl acrylate in these four solvents, and carbon tetrachloride is the poorest solvent.

The gradient of the lines in Fig. 2 is identified with C_2, and this can be regarded as zero from this figure. The value of C_2 can be considered to show the degree of the restriction to the possible configuration of the molecular chain, and therefore those solvents, in which the interaction forces between long chain molecules can be considered to be fairly loosen, are good.

Doty and Zable7) showed that $\mu=0.55$ is the border-line between poor solvent and non-solvent. Huggins8) showed that $\mu=0.50$ is the border-line between poor and good solvent. Further, in the case of gel, μ depends upon the concentration of cross-linking agent9). On the other hand, the different values of μ for the same polymer-solvent system are reported by the different workers, even if the values are determined mechanically by the same method2).

In this experiment, from the considerations on the values of v_r, μ or C_2, the author has assumed that chloroform, benzene and toluene are good solvents and carbon tetrachloride is a poor solvent. The values of μ obtained at 31, 25 and 15°C seem to show, also, that benzene is a good solvent**.

From the accuracy in the determination of μ, especially from its temperature dependency, the results obtained in this experiment are not enough to be discussed in detail. There are also some questions concerning the effect of cross-linking agent as mentioned above. However, the values of μ obtained here seem to be not so unreasonable compared with the other workers' results.

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8) M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **44**, 431 (1943).

9) R. F. Boyer and R. S. Spencer, *J. Polym. Sci.*, **3**, 97 (1948).

** These values are; $\mu_{31}=0.51_6$; $\mu_{25}=0.51_3$; $\mu_{15}=0.50_9$.