The Mechanical Behavior of Swollen Polymethyl Acrylate Gels. III. Thermoelastic Properties of Swollen Gels

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When a gel is in equilibrium with a solvent, the degree of swelling and its mechanical properties depend upon the intermolecular interaction. This is shown in the preceding paper[1] for the phenomena of stress relaxation.

Gee investigated the effect of several kinds of solvent upon the elasticity of rubber[2], and pointed out that the elasticity observed in his experiment does not always coincide with the result expected from statistical theories proposed by Flory, or James and Guth[3].

Continuing from the preceding paper, the author has observed the temperature dependence of the elastic behavior of polymethyl acrylate gel in two kinds of solvent which have different powers for the polymer.

The external force of extension f is expressed as

$$f=(\partial G/\partial l)_T$$

when the volume dose not change during the deformation, where G is free energy and l is the length of the body.

As the entropy S is $S=-(\partial G/\partial T)_l$, one may write $(\partial S/\partial l)_T=-(\partial f/\partial T)_l$.

The thermodynamical relation can be expressed as,

$$(\partial G/\partial l)_T=(\partial H/\partial l)_T+T(\partial f/\partial T)_l$$

or

$$(\partial H/\partial l)_T=f-T(\partial f/\partial T)_l$$

where H is the enthalpy.

Using the extension ratio $\alpha=l/l_0$, where l_0 is the initial length, the following relation can be deduced.

$$(\partial G/\partial\alpha)_T=fl_0 \tag{1}$$

$$(\partial H/\partial\alpha)_T=fl_0-Tl_0(\partial f/\partial T)_\alpha \tag{2}$$

$$T(\partial S/\partial\alpha)_T=(\partial H/\partial\alpha)_T-(\partial G/\partial\alpha)_T \tag{3}$$

The equation 1 gives the relation between free energy change and extension ratio α when the force under the various extensions at a constant temperature is measured for a sample which has the initial length l_0; the equation 2 gives the relation to obtain the enthalpy change from the temperature dependence of force at a constant extension ratio and the values of fl_0. From equation 3 combined with equation 1 and 2, we obtain the entropy change.

Experimental

The apparatus to observe the change in force with extension is the same one as used in the previous paper[4] (cf. Fig. 1 in the reference 4). Sample is polymethyl acrylate gel, cross-linked diallyl adipate and swollen in carbon tetrachloride and benzene; the former is a poor and the latter is a good solvent as reported in the previous papers[1,4]. The stress-strain relations observed at constant temperatures are shown in Fig. 1 or Fig. 2, where the strain means the compression and the stress is the initial stress. These curves are drawn connecting the observed points by a smooth line. Some deviations of these points from the smooth curve were observed. Gee supposed that these deviations may be due to the stress relaxation in the sample[2].

It must be noticed that the initial length l_0 itself changes with variation of temperature. To give the *same* extension ratio to the sample at different temperatures, the amount of compression for the sample must be changed corresponding to each temperature. In practice, the contact (G and G' in the Fig. 1 of the reference 4) is adjusted for each run to touch slightly, and therefore the change of stress which originated from the change of initial length, l_0, by thermal expansion is cancelled by this operation, then some definite compression which is determined from the initial length of the sample at the standard temperature (30°C) is given, and the corresponding stress is measured. It seems to be more correct to assume that the value of the strain imposed on the sample is adjusted according to the linear thermal expansion of the sample. But it has not been taken into account to perform this calibration in the present experiment, because, owing to the change in the length accompanying the temperature change, precise determination of the dimension of the sample is not possible*.

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[1] K. Ogino, This Bulletin, **31**, 580 (1958).

[2] G. Gee, *Trans. Faraday Soc.*, **42**, 585 (1946).

[3] P. J. Flory, *J. Chem. Phys.*, **11**, 521 (1943).
H. M. James and E. Guth, ibid. **11**, 455 (1943).

[4] K. Ogino, This Bulletin, **31**, 577 (1958).

* Physical meaning of this thermal expansion is discussed in reference 2.

The temperature dependency of the stress is determined from the values at several strains on each curve in Fig. 1 or Fig. 2. The results are shown in Fig. 3 and Fig. 4.

$(\partial f/\partial T)_\alpha$ is calculated by multiplying the slopes of each curve in Fig. 3 or Fig. 4 by the cross sectional area of the specimen. Also we obtain $(\partial G/\partial\alpha)_T$ from f and l_0 for each extension ratio at constant temperature. $(\partial H/\partial\alpha)_T$ and $T(\partial S/\partial\alpha)_T$ can be calculated from these values with equations 2 and 3. $(\partial G/\partial\alpha)_T$, $(\partial H/\partial\alpha)_T$ and $T(\partial S/\partial\alpha)_T$ per cubic centimeter can be obtained by dividing these values by the volumes of each specimen.

Results and Discussion

Fig. 5 and Fig. 6 are the curves which show the calculated values of $(\partial G/\partial\alpha)$, $(\partial H/\partial\alpha)$ and $T(\partial S/\partial\alpha)$ at 30°C in these two solvents. In practice, $T(\partial S/\partial\alpha)$ is obtained graphically from the difference between $(\partial G/\partial\alpha)$ and $(\partial H/\partial\alpha)$. Free energy change at constant temperature and pressure equals the external work, and enthalpy change at constant pressure equals the change of internal energy when no volume change occurs. Fig. 5 and Fig. 6 show the direction of the change of G, H and S when strain, or α, increases.

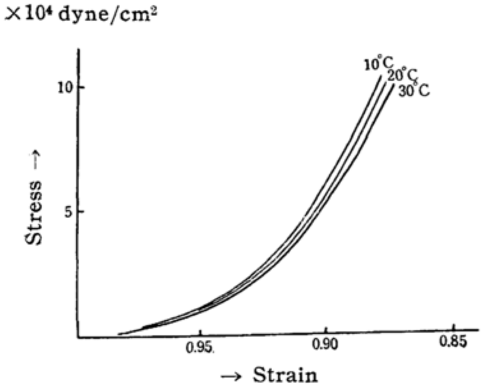

Fig. 1. The stress-strain curves for carbon tetrachloride.

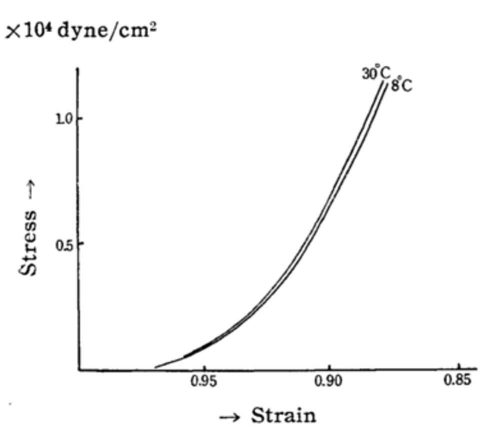

Fig. 2. The stress-strain curves for benzene.

Carbon tetrachloride is not a good solvent for polymethyl acrylate considering the degree of swelling or other experimental results, as reported in the previous papers. In this solvent, $(\partial S/\partial\alpha)$ has a positive value for increasing of α, and so the

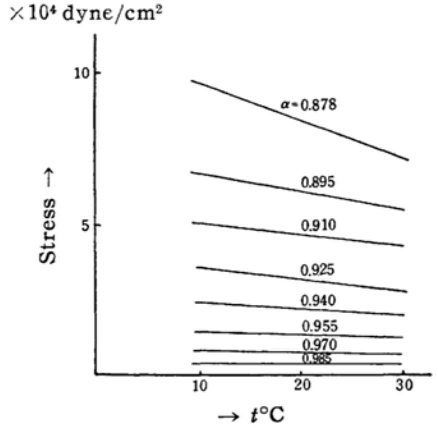

Fig. 3. The stress-temperature curves for carbon tetrachloride.

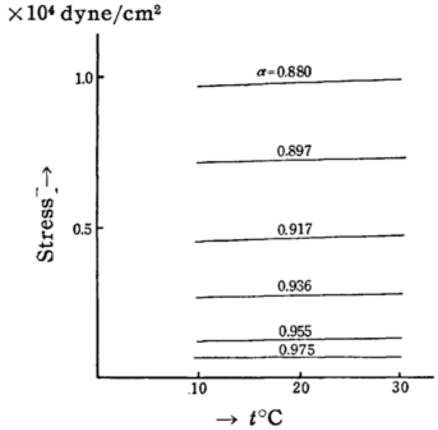

Fig. 4. The stress-temperature curves for benzene.

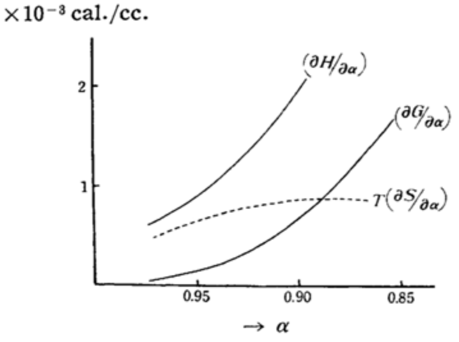

Fig. 5. Thermodynamics of compression for carbon tetrachloride.

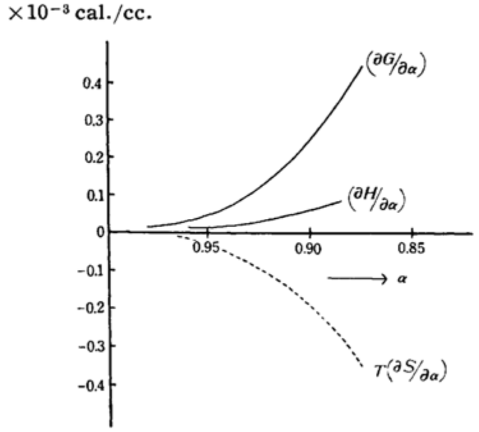

Fig. 6. Thermodynamics of compression for benzene.

magnitude of this entropy change increases with the increase of strain. Enthalpy change ($\partial H/\partial\alpha$) is also positive, thus the change of internal energy increases with the increase of strain.

On the contrary, in benzene, polymer swells to a great extent, and in this case, with the increase of strain, the degree of the change of internal energy (positive, in this case) is not so large, and ($\partial S/\partial\alpha$) is negative; i. e., the magnitude of entropy change decreases with increase of strain.

The increase of internal energy with extension would correspond to the fact that the external work is stored as potential energy between molecules.

In a poor solvent, like carbon tetrachloride, intermolecular interaction exists to a considerable degree, as expected from the above results. In this case, external force may loose to some extent the cohesion between molecules, and the increase of randomness of polymer molecules or the releasing of solvent molecules fixed around the polymer chains contributes to the increase of entropy of the system. These aspects seem to be acceptable from the fact that the degree of stress relaxation is more remarkable in a poor solvent, and that each parameter in four-element model is larger compared with the values obtained for a good solvent.

In the case of benzene, which is a good solvent, the decrease in entropy change is much higher than the increase in internal energy change. This may originate from the fact that the restriction for free rotation or flexion of chain molecules is removed by the high degree of swelling, and that the freedom of chain molecules is expected to decrease with the increase of strain.

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