The Mechanical Behavior of Swollen Polystyrene, Poly-p-chlorostyrene and their Copolymers in Benzene. I. The Degree of Polymer-solvent Interaction and Thermoelastic Properties

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In the previous papers[1], the influence of the polymer-solvent interaction upon the mechanical properties of the swollen polymethyl acrylate gels was discussed, and it was shown that the mechanical properties of these gels having various degrees of swelling can be interpreted as the function of the interaction force between polymer chains. The intermolecular force between chain polymers was controlled, however, by giving the different degrees of swelling through the use of several organic solvents of different solvent power.

It is interesting to examine, in the next step, how the mechanical properties of gels in a swelling equilibrium with solvents are influenced by the structural units in a polymer molecule.

In this paper, polystyrene, poly-*p*-chlorostyrene and their copolymers, slightly cross-linked with divinyl benzene, are carried into the swelling equilibrium in benzene, and the mechanical properties of these gels are studied.

At the swelling equilibrium with excess solvent, the following equation holds[2]

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

where v_r is the volume fraction of polymer, ρ the density of pure solvent, V_0 the molar volume of solvent, M_c the average molecular weight of polymer between junction points and μ a parameter which indicates the type and degree of interaction exhibited by the polymer-liquid system.

In the region in which the stress-strain curve is reversible, the force f required to extend a specimen to an extension ratio λ is given by[3]

$$f=2Av_r^{-1/3}(\lambda-\lambda^{-2})(C_1+\lambda^{-1}C_2) \qquad (1)$$

where A is an unstrained area of cross section in the dry state, and C_1 and C_2 are the parameters relating to the mechanical properties of the specimen.

At a high degree of swelling, we can obtain the following relation from statistical consideration,

$$C_1=1/2\boldsymbol{RT}M_c^{-1}$$

From these relations, the next equation follows,

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

Thus, we can estimate the value of C_1 from Eq. 1 by plotting the value of $f\{2A_0(\lambda-\lambda^{-2})\}^{-1}v_r^{1/3}$ against λ^{-1} in the results of the stress-strain measurements, and then can obtain the parameter μ from Eq. 2 using this value of C_1.

On the other hand, the following thermodynamic relations can be deduced.

$$(\partial G/\partial\lambda)_T=f\,l_0 \qquad (3)$$

$$T(\partial S/\partial\lambda)_T=-Tl_0(\partial f/\partial T)_\lambda \qquad (4)$$

$$(\partial H/\partial\lambda)_T=T(\partial S/\partial\lambda)_T+(\partial G/\partial\lambda)_T \qquad (5)$$

where G is the freee energy, H the enthalpy and S the entropy. From the above relations, we can estimate the change of the thermodynamic functions by measuring initial stresses at various strains and temperatures.

Experimental

Samples.—Commercial monomeric styrene and divinyl benzene were purified by fractional distillation under the reduced pressure after the removal of inhibitor with aqueous alkaline solution.

Benzene was purified by the ordinary method.

p-Chlorostyrene was synthesized in the following way[4]. Purified commercial mono-chlorobenzene reacts with acetyl chloride in the presence of aluminum chloride (Friedel-Crafts' reaction), and the *p*-chloroacetophenone thus obtained was reduced to *p*-chloro-phenylmethylcarbinol by isopropyl alcohol saturated with aluminum isopropylate prepared freshly before

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[1] K. Ogino, This Bulletin, **31**, 577, 580, 584 (1958).

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

[3] R. S. Rivlin and D. W. Saunders, *Phil. Trans.*, **A243**, 251 (1951).

[4] E. Matui, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **45**, 1094 (1942).

the reaction. Finally this carbinol was dehydrated by potassium bisulfate in the presence of picric acid⁵⁾ under reduced pressure.

Six cc. of styrene, or *p*-chlorostyrene or a mixture of these two monomers was polymerized with about 0.01 cc. of divinyl benzene in bulk in a sealed glass tube by the method described in the previous paper¹⁾.

The polymer block was then cut into several parts about 1 cm. in length by a turning lathe. Care was taken so that the error in the diameter of the specimen was confined within 10^{-3} cm. These polymer rods were then dipped in the excessive amount of benzene, and brought into the swelling equilibrium.

Apparatus. — The apparatus used in this experiment is the same as that used in the previous experiment¹⁾, and is shown in Fig. 1.

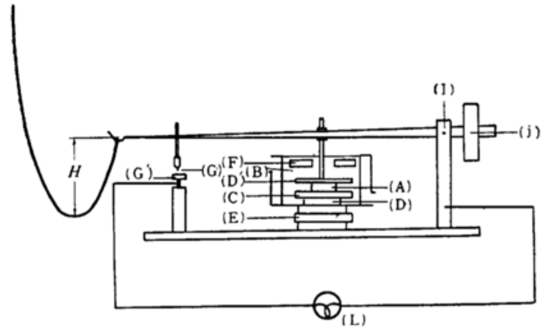

Fig. 1. The apparatus used in this experiment. (A), Specimen; (B), Solvent; (C), Iris; (D), Pressure plate; (E), Screw; (F), Desiccating agent; (G & G'), Contact; (J), Balancing weight.

The specimen in the swelling equilibrium with the solvent is placed between a flat brass block (D) and a pressure plate (D') in the solvent, and is strained vertically to a given extent, by rotating the screw (E) which is graduated to 1/100 mm. The initial stress is measured by the chain (H) using the value of its linear density.

The temperature of the specimen was controlled by circulation of water within the range of ±0.5°C.

Results and Discussion

The plot of $f\{2A(\lambda-\lambda^{-2})\}^{-1}v_r^{1/3}$ against λ^{-1} at 25°C is shown in Fig. 2, and the values of μ for each polymer are given in Table I.

TABLE I. THE VALUE OF μ IN BENZENE AT 25°C

Polymer	μ
Polystyrene	0.47
Poly-*p*-chlorostyrene	0.49_5

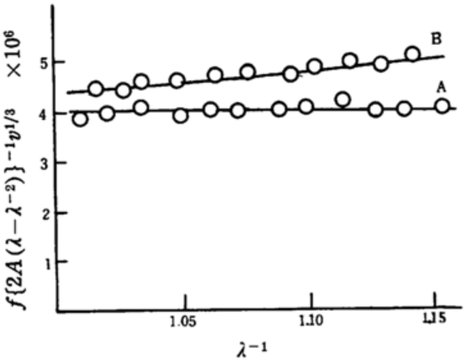

Fig. 2. Diagram of $f\{2A(\lambda-\lambda^{-2})\}^{-1}v_r^{1/3}$ against λ^{-1} for polystyrene-benzene (A) and poly-*p*-chlorostyrene-benzene (B) at 25°C.

The thermodynamic quantities in Eqs. 3, 4 and 5 at 25°C are shown in Figs. 3—6.

The value of μ of 0.47 for the system polystyrene-benzene differs from the value 0.453 by Boyer and Spencer⁶⁾ in their study of the stress-strain properties of this system.

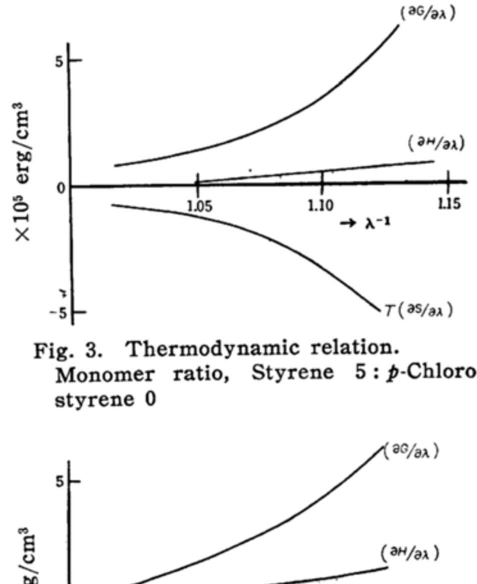

Fig. 3. Thermodynamic relation. Monomer ratio, Styrene 5 : *p*-Chlorostyrene 0

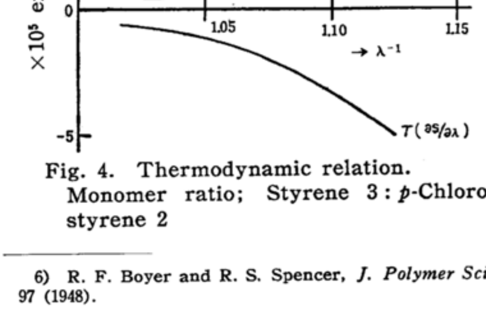

Fig. 4. Thermodynamic relation. Monomer ratio; Styrene 3 : *p*-Chlorostyrene 2

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5) H. R. Snyder et al., "Org. Syntheses", Vol. 28, John Wiley & Sons, New York (1948), p. 31.

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

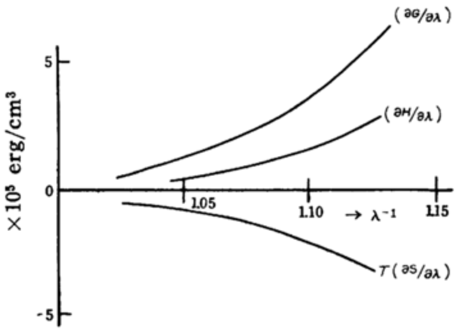

Fig. 5. Thermodynamic relation. Monomer ratio; Styrene 2 : *p*-Chlorostyrene 3

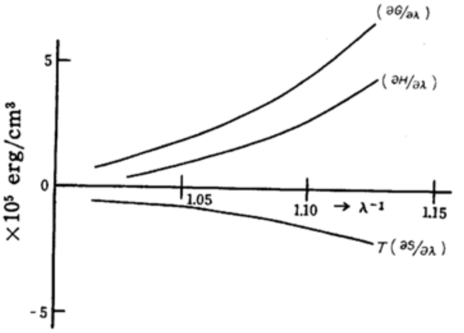

Fig. 6. Thermodynamic relation. Monomer ratio; Styrene 0 : *p*-Chlorostyrene 5

Such a difference as this is also found among the other workers: Rivlin et al.[7] obtained the value of μ of 0.42 for natural rubber-benzene, and compared it with the value of 0.395 reported by Gee*. These two values were obtained from the stress-strain measurement of swollen rubbers. The measurements were conducted in ways similar to each other. Rivlin et al. considered that the source of the larger value of μ obtained in their investigation might be due to the degradation of the rubber during prolonged swelling in solvent in the determination of v_r.

An alternative source for the discrepancy in the values of μ originates from the effect of cross-linking as mentioned in the previous paper[1].

The fact that the value of μ of poly-*p*-chlorostyrene (0.49_5) is greater than that of polystyrene (0.47) shows that benzene is not so good a solvent for poly-*p*-chlorostyrene as for polystyrene. This may be due to the substituted chlorine atoms, for there appears a large polarity, and greater interaction may arise between long chain molecules. Thus, polymer-polymer contacts increase by the presence of chlorine atoms, and hence μ becomes larger.

The gradient of the curves of $f\{2A(\lambda-\lambda^{-2})\}^{-1}v_r^{1/3}$ against λ^{-1} is identical with C_2. It is well known that[3] the value of C_2 depends on the degree of swelling, v_r, and is found to be independent of the nature of the rubber polymer, the degree of vulcanization, and of the nature of the swelling liquid. It is associated primarily with the existence of secondary network. The experimental data in Fig. 2 shows a good linear relationship for these two polymers, and the gradients of these two lines, or C_2, are nearly equal to zero. But if we compare poly-*p*-chlorostyrene gel with polystyrene gel, the former has a slightly larger positive value of C_2. From this fact, it is reasonable to assume that the larger restriction to the possible configuration of the molecular chain exists in poly-*p*-chlorostyrene gel, and so the interaction force between long chain molecules can be considered to be stronger.

Deutsch, Hoff and Reddish[8] and also Scott and Magat[9] discussed the effect of some polar groups upon the mechanical and dielectric properties, or upon the cohesive energy density of polymer, and their results support the above consideration**.

The strength of intermolecular force between chain molecules is also estimated from the change of thermodynamic functions. The increase of chlorine content in copolymers corresponds to the large contribution of the term $(\partial H/\partial\lambda)$ to $(\partial G/\partial\lambda)$. The function H can be considered as the internal energy, and the large value of a change of this term may be due to the strong interaction between chlorine atoms, i.e., the change of internal energy when a strain increases is increased by the introduction of a stronger intermolecular force. As these systems are in the same solvent and have a nearly equal volume fraction v_r, we can assume that

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

* Gee has also reported the other value of μ of 0.41 from the vapor pressure measurement. Cf., *Trans. Faraday Soc.*, **42**, 507 (1946).

[8] K. Deutsch, E. A. W. Hoff and W. Reddish, *J. Polymer Sci.*, **13**, 565 (1954).

[9] R. L. Scott and M. Magat, ibid., **4**, 555 (1949).

** The structural effect upon the melting point or freezing point has been summarized by Uematu. Cf., *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **59**, 750 (1956).

the change of the value of μ or of thermodynamic functions comes from the presence of chlorine atoms.

In the present discussion, the author considered that the effect of chlorine atoms may prevail upon their volume effect in relation to the mechanical properties, and took into account only this effect. But, of course, there must exist some volume effect of this polar group, and this is neglected in the above discussion.

The effect of intermolecular forces upon the other mechanical properties by introducing chlorine atoms is now under study.

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