The Mechanical Behavior of Swollen Polystyrene, Poly-p-chlorostyrene and their Copolymers in Benzene. II. Stress Relaxation under Constant Strain

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In the previous paper[1], the stress relaxation of swollen polymethylacrylate gels in several organic solvents was studied, and it was shown that the smaller the volume fraction of polymer is, the greater degree of relaxation, and the higher temperature dependency of stress relaxation are observed.

In this paper, the stress relaxation of gel swollen in benzene is studied as a function of intermolecular force which is controlled by changing the content of substituted chlorine atoms in the chain molecules[2].

When a viscoelastic body is strained quickly to a definite extent and kept at this state, the relaxation of stress is observed.

Tobolsky et al. have shown[3] that the relaxation curves at different temperatures can be superposed upon each other when plotted as the reduced stress, g, against the logarithmic time, and that a change in temperature corresponds to a shift of the curve along the logarithmic time scale. (In the present experiment, the stress is arbitrarily reduced to 20°C, and is denoted by g_{20}.)

The existence of this superposition principle of relaxation curves at different temperatures indicates that the relaxation curves for the same polymer at different temperatures are identical if plotted as the reduced stress vs. the logarithm of (Kt) where K is a function of temperature. Or we can express the reduced stress g_{20}, for example, as a function of Kt[3]; i. e.,

$$g_{20} \equiv g_{20}(Kt)$$

It is found that the temperature dependence on K may be expressed by Arrhenius's equation[3]

$$K = A\,\exp.\,(-H/\boldsymbol{R}T)$$

The apparent activation energy H can therefore be calculated by plotting the logarithm of the time factor K against the reciprocal of absolute temperature.

Experimental

Samples.—About 4 cc. of styrene (for sample A), p-chlorostyrene (for sample D) or their mixtures (for samples B and C) which contains one drop (about 2 mg.) of divinylbenzene and about 10 mg. of benzoyl peroxide was polymerized thermally in bulk in a sealed glass tube. They were swollen in

TABLE I. VOLUMES OF STYRENE AND p-CHLOROSTYRENE MONOMER TAKEN INTO POLYMERIZATION

Sample	p-Chlorostyrene, cc.	Styrene, cc.
A	0	4
B	1.6	2.4
C	2.4	1.6
D	4	0

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[1] K. Ogino, This Bulletin, 31, 580 (1958).
[2] K. Ogino, ibid., 32, 553 (1959).
[3] A. V. Tobolsky et al., *J. Polymer Sci.*, 3, 669 (1948).

benzene to the equilibrium state. Benzene was purified by shaking several times with concentrated sulfuric acid, and with distilled water, and was then dried over calcium chloride and redistilled.

Volumes of *p*-chlorostyrene and styrene monomer before polymerization are shown in Table I.

Apparatus. — The apparatus used to observe the change of stress with time is the same as was described in the previous paper¹⁾, and is shown in Fig. 1; a definite strain (11.2%) is given to the specimen (A) and the stress, measured by the vertical component of the chain length, is recorded on a rotating drum. The chain corresponding to and following the decaying stress at each time is controlled by a balancing motor (E) which is connected to a relay (F) through an amplifier circuit (G).

Results and Discussion

The experimental curves of the reduced stress against logarithmic time for each polymer are shown in Figs. 2, 3, 4 and 5.

The apparent activation energy for the relaxation obtained by plotting the logarithm of the time factor K against the reciprocal temperature is also shown in each figure.

If these curves at different temperatures are superposed with each other by suitable translations along the logarithmic time axis, the master curves shown in Fig. 6 are obtained.

Four parameters in the mechanical model¹⁾

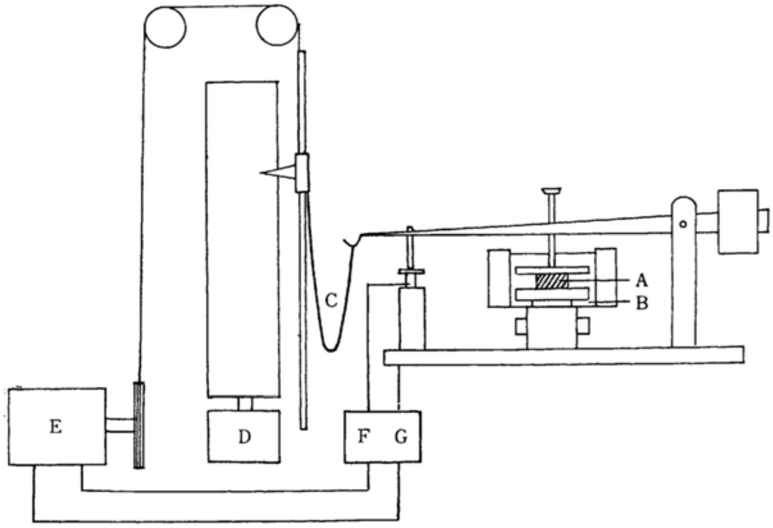

Fig. 1. Chainomatic balance.

(A): Specimen (B): Solvent (C): Chain (D): Rotating drum
(E): Balancing motor (F): Relay (G): Amplifier circuit

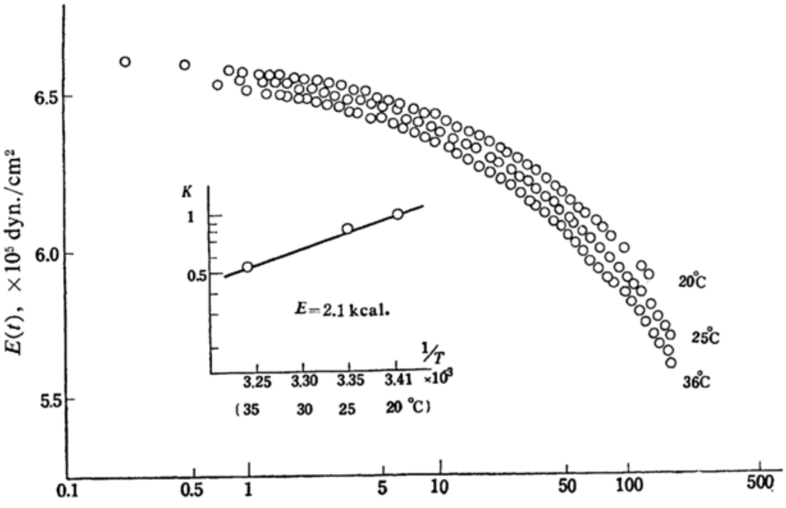

Fig. 2. Stress relaxation curves for sample A, E=2.1 kcal.

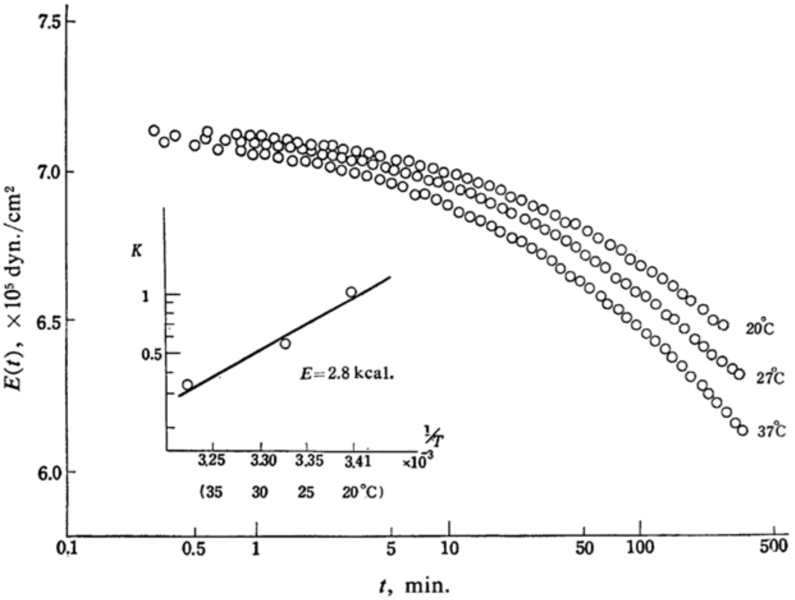

Fig. 3. Stress relaxation curves for sample B, E=2.8 kcal.

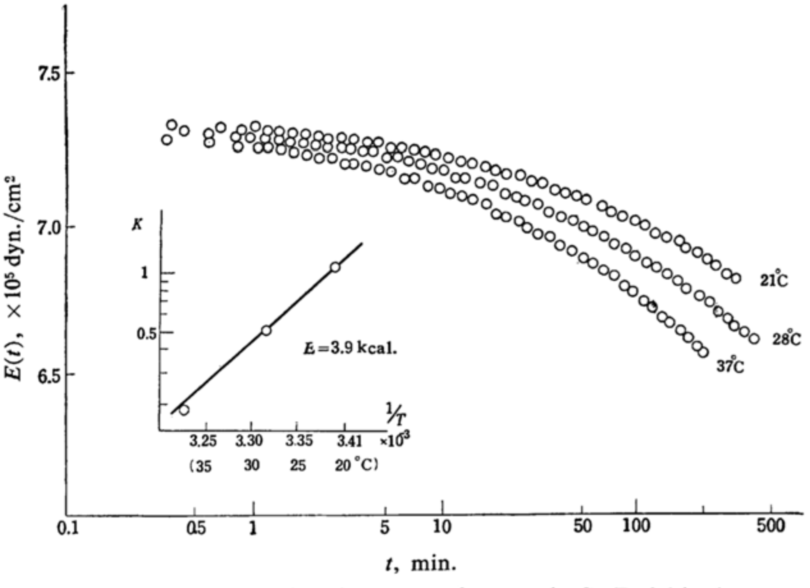

Fig. 4. Stress relaxation curves for sample C, E=3.9 kcal.

to express the curves of Fig. 6 are listed in Table II.

As these gels are cross-linked chemically by divinylbenzene, we can expect that the stress relaxation in the present case arises mainly from the breakage or slippage of some weak bonds such as entanglements or other secondary bonds present between junction points.

The value of G_1, in Table II, increases with the increase of chlorine content. Considering that these gels have nearly equal values of v_r, volume fraction of polymer at swelling equilibrium⁽4⁾, the fact that the initial Young's modulus G_1 increases with the increase of chlorine content leads to the assumption that the stronger interaction force between chain molecules appears by the presence of chlorine atoms.

As each parameter in the four-element model for the chlorine rich gel, especially η_2 or η_3, is large, we can assume that the contribution of chlorine atoms to the relaxation or viscous

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

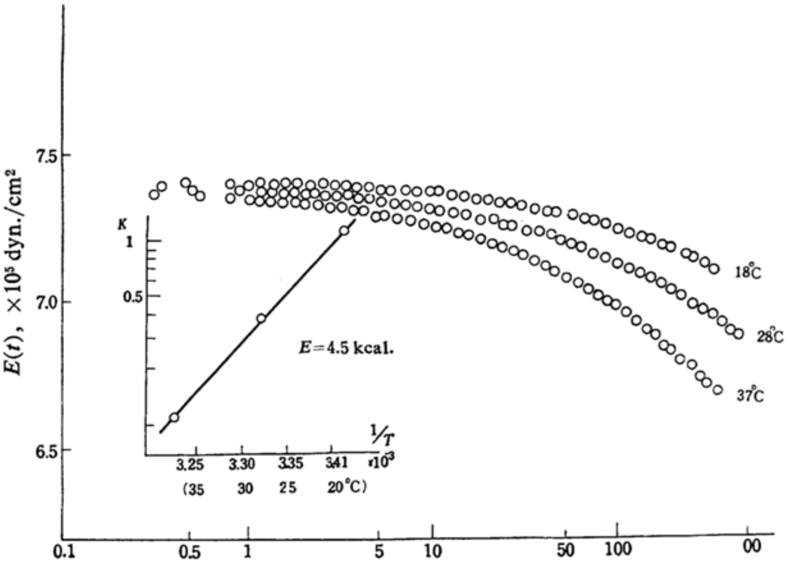
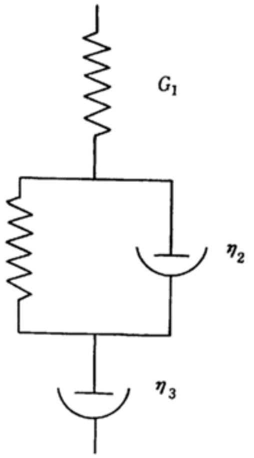


Fig. 5. Stress relaxation curves for sample D, E=4.5 kcal.

TABLE II. PARAMETER VALUES IN FOUR-ELEMENT MODEL

Sample	v_r	G_1 dyn./cm^2	G_2 dyn./cm^2	η_2 (poise)	η_3 (poise)	η_3/G_1, sec.	η_2/G_2, sec.
A	4.3	5.90×10^6	2.54×10^8	3.90×10^8	8.55×10^{11}	1.45×10^5	1.5
B	4.1	6.35×10^6	7.50×10^7	4.70×10^8	3.75×10^{12}	5.95×10^5	6.7
C	4.0	6.54×10^6	1.23×10^8	2.39×10^9	3.35×10^{12}	5.12×10^5	19.4
D	4.4	6.63×10^6	3.00×10^8	2.95×10^9	3.99×10^{12}	6.03×10^5	10



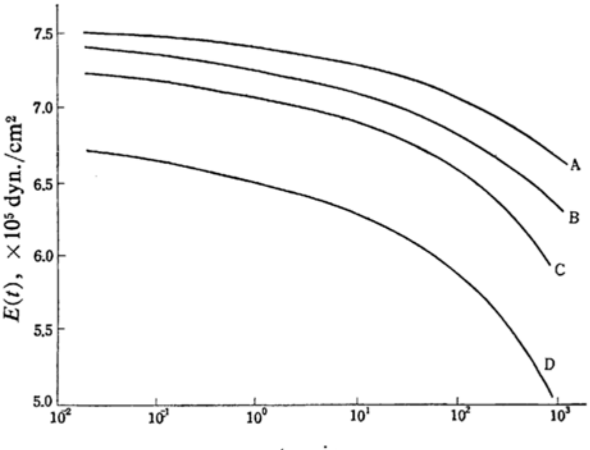


Fig. 6. Relaxation master curves.

property is, primarily, a decisive factor.

When we express these mechanical properties by this four-element model, the value of the retardation time η_2/G_2 can be expected to have a comparable value to the observation time scale, and values of these parameters in Table II can be considered to be reasonable from this point.

Hatfield and Rathmann assumed[5] that for swollen gels viscous flow or molecular slippage is brought about by chemical rupture of primary bonds. For the fact that η_2/G_2 in Table II has the order of about 10° sec., the author assumed that the retardation time of this order

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[5] M. R. Hatfield and G. B. Bathmann, *J. Appl. Phys.*, 25, 1082 (1951).

may correspond to the slippage of some secondary bonds in polymeric substances.

The values of η_3 in the four-element model for the other polymeric substances are much smaller than that of this gel (about 10^7 poises is expected in the usual case). This parameter may be considered to correspond to a process of a longer retardation time. It will be possible to consider that for swollen gels most of the secondary bonds are set free by solvation, and that the number of bonds which are to slip off or to be liberated per unit time under constant strain are much fewer than those in the dry and undiluted states. The apparent rate of flow will therefore be smaller, and the viscosity will then be much greater (10^{12} poises).

The apparent activation energy for relaxation process is also great when the chlorine content increases. The great activation energy means great temperature dependence. As the contribution of energy term to the elasticity or the value of μ, polymer-solvent interaction parameter4), increases with the increase of chlorine content2), we can presume that the cause of the great temperature dependence may be the fact that the breaking of some secondary bonds are favored because the solvent-polymer contacts increase, or that these bonds come to be slipped off more easily as temperature rises. In the case of polystyrene gel, on the other hand, there may be no residual secondary bonds to be released by temperature rise.

These facts can be interpreted by considering the appearance of the interaction force by the introduction of chlorine atoms, as was mentioned here and in the previous paper2).

In this discussion, the author considered that the nature of the solvent itself has no influence upon the relaxation phenomena of swollen gels, as it may not be affected by the different content of chlorine atoms in the swollen gels.

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