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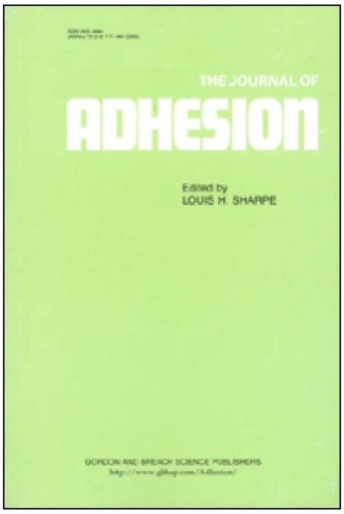

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# Contact Angles on Swollen Polymers: The Surface Energy of Crosslinked Polystyrene

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The contact angle of $CH_2I_2$, α-bromonaphthalene and aniline on crosslinked polystyrene has been measured. The polymer was swollen for as long as 60 days in the liquid whose contact angle was to be measured. The surface free energy, $\gamma_s$, of unswelled polystyrene was estimated from the contact angles and the swelling results, using an equation which had previously been proposed by Good. The value of $\gamma_s$ is estimated to be $42 \pm 2$ ergs/cm$^2$.

## INTRODUCTION

The wetting of a solid by a liquid which swells it is a subject which has not received quantitative, experimental attention, up to the present. Adam[1] has pointed out that the contact angle should decrease with swelling by the wetting liquid. The surface free energy of a low-energy solid which is not swelled can be estimated from the contact angle which liquids form on the solid[2–4] by means of the equation,

$$\gamma_s = \frac{\gamma_l(1+\cos\theta)^2}{4\Phi^2} \tag{1}$$

where $\theta$ is the contact angle formed by the liquid whose surface tension is $\gamma_l$, and $\Phi$ is an interaction parameter for that liquid with the solid. $\Phi$ can be

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evaluated from molecular properties of the two phases.[3, 4] Eq. (1) is valid when the equilibrium film pressure, $\pi_a$, is negligible; this approximation is probably valid for most smooth, homogeneous, low-energy solids.[5] It has been shown[2–4, 6] that $\gamma_s$ is approximately equal to $\gamma_c$, the critical surface tension for wetting[7]:

$$\gamma_c = \Phi^2\gamma_s \tag{2}$$

Polystyrene has been studied by Zisman and his co-workers,[8, 9] with ambiguous results regarding $\gamma_c$. Two parallel straight lines were reported in the plot of $\cos\theta$ *vs* $\gamma_l$: one for hydrogen bonding liquids, and another for non-hydrogen bonding substances such as $CH_2I_2$. Zisman *et al.* preferred the value of $\gamma_c$ equal to 33 ergs/cm$^2$, obtained with the former series, no doubt because of uncertainty as to the values of $\theta$ found with the latter. Liquids in the latter group swell polystyrene (they eventually dissolve it) at a rate such that an experimenter would be justified in having less than full faith in the measured angles. See Ref. 4 for a further discussion of the extrapolation made with hydrogen bonding liquids.

A solution to the experimental difficulty in measuring contact angles of liquids such as $CH_2I_2$ on polystyrene is to crosslink the polymer, and measure the contact angle on the solid which had been allowed to swell to equilibrium in the liquid whose contact angle is to be measured. Good has shown[6] that the following treatment can be used: for two substances, 1 and 2, whose mutual solubilities are high, we define the volume fraction-weighted averages of the surface free energies:

$$g_a \equiv \phi_1^a\gamma_1+\phi_2^a\gamma_2 \tag{3a}$$

$$g_b \equiv \phi_1^b\gamma_1+\phi_2^b\gamma_2 \tag{3b}$$

Here $\phi_1^a$ is the volume fraction of substance 1 in phase *a*, and $\phi_2^a$ is the volume fraction of substance 2 in that phase. $\phi_1^b$ and $\phi_2^b$ are defined similarly, with respect to phase *b*. For a crosslinked polymer, swelled in liquid *l*, the volume fraction of polymer, $\phi_s^l$, in the liquid is negligible; and we can write

$$g_s = \phi_s^s\gamma_s+\phi_l^s\gamma_l$$

$$g_l \doteq \gamma_l$$

The interaction parameter, $\Phi_{sl}$, will be approximately unity, because the cohesive energy densities of the two phases must be close together if swelling is to be appreciable.

The contact angle equation, then, becomes

$$\cos\theta = -1+2\left(\frac{g_s}{g_l}\right)^{\frac{1}{2}} \tag{4a}$$

$$= -1+2\left(\phi_l^s+\phi_s^s\frac{\gamma_s}{\gamma_l}\right)^{\frac{1}{2}} \tag{4b}$$

We can now solve Eq. (4b) and write the equation which corresponds to Eq. (1):

$$\gamma_s = \frac{\gamma_l}{\phi_s^s}\left[\frac{(1+\cos\theta)^2}{4} - \phi_l^s\right] \tag{5}$$

The value of $\gamma_s$ obtained by this method is the surface free energy of the unswelled polymer. Eq. (4) leads to the qualitative prediction that $\theta$ will be lower for a particular liquid on a polymer that is swelled by the liquid, than it would be on the same polymer if it were not swelled.

## EXPERIMENT

Crosslinked polystyrene was prepared by polymerization in contact with glass, with mercury, and with nitrogen. Concentrations of 1 to 5% divinylbenzene (DVB) were used. The preparation in glass was made in Sauereisen-cemented glass cells, about 5 mm thick and 8.5 x 10 cm, open at one end. The polymer pulled away from the glass spontaneously, near the end of the polymerization. At the end of the reaction, the cell was broken to free the sample. The mercury- and $N_2$-contact preparation was made by floating the styrene-DVB solution on mercury, in the bottom of cylindrical bottles which were about 4.5 cm in diameter, with dry $N_2$ over the liquid. At the end of the polymerization, the bottles were carefully broken, to get at the polymer.

The initiator was azo-bis-butyronitrile. Commercial styrene and DVB were freshly distilled under nitrogen, for each preparation. Dry $N_2$ was bubbled through the reaction mixture before it was heated to the reaction temperature, which was 50°C. About 50 to 60 hours were required for the reaction; a stream of $N_2$ over the polymerizing liquid was maintained during this step.

Samples about 1 to 2 cm square were cut from the slabs of polymer, and were placed in the swelling liquids. The liquids were Reagent grade $CH_2I_2$, $\alpha$-bromonaphthalene, and aniline; the former two were purified by passing through adsorption columns of activated $SiO_2$ or $Al_2O_3$; the aniline was treated with activated carbon. From time to time, the samples were removed from the liquids, and blotted dry and weighed. The contact angles were determined using fresh liquid in each case.

The contact angles were measured by the sessile drop-goniometer method, using a Kernco contact angle instrument. The drops were placed on the surface with the aid of a micropipet. Advancing angles were measured. Retreating angles of the organic liquids were, in every case, low (or zero) and poorly reproducible. Measurements were made with the least possible delay, so as to minimize evaporation and consequent deswelling.

## RESULTS

Figure 1 shows the per cent swelling of polystyrene containing 5% DVB, in $CH_2I_2$, as a function of time; it also shows the volume fraction, and the contact angle. Swelling equilibrium appeared to have been reached after about 30 days, and the steady state contact angle was attained in perhaps a little shorter time than that. The other samples showed a similar time dependence. Figure 2 shows the volume fraction swelling and the contact angle for α-bromonaphthalene. The angle reached zero in 9 days. Aniline behaved similarly to α-bromonaphthalene, except for a somewhat greater rate of swelling and decrease in $\theta$.

TABLE I

Limiting contact angles of $CH_2I_2$ on swelled polystyrene, and computed values of $\gamma_s$

| Contact surface during polymerization | % DVB | Equilibrium swelling, volume fraction $\phi_s^s$ | Equilibrium advancing contact angle degrees | Computed $\gamma_s$, ergs/cm$^2$ |
|---|---|---|---|---|
| Mercury | 5 | 0.250 | 18 | 41 |
| | 3 | 0.249 | 18 | 42 |
| | 2 | 0.248 | 12 | 49.5 |
| $N_2$ | 5 | 0.250 | 15 | 44 |
| | 3 | 0.249 | 17 | 42 |
| Glass | 4 | 0.279 | 27 | 35.5 |
| | 3 | 0.270 | 23 | 36 |
| | 2 | 0.254 | 16 | 43 |
| | 1 | 0.231 | 18 | 40 |

Figure 3 shows the computed value of $\gamma_s$, obtained by use of Eq. (5), from $CH_2I_2$ contact angles on the swelled 5% DVB polymer. The value, 50.8 dynes/cm, was used for the surface tension of $CH_2I_2$. A similar trend was found with all five concentrations of DVB in the polymer, and with all three types of surfaces.

Table I shows the limiting values of $\gamma_s$, computed for the five different samples, from the $CH_2I_2$ contact angles. No limiting values are reported for 1 or 2% DVB surfaces formed in contact with $N_2$, or 1% DVB surface formed on Hg, because as the swelling progressed, the surface became so rough that its texture could easily be seen without magnification, and the

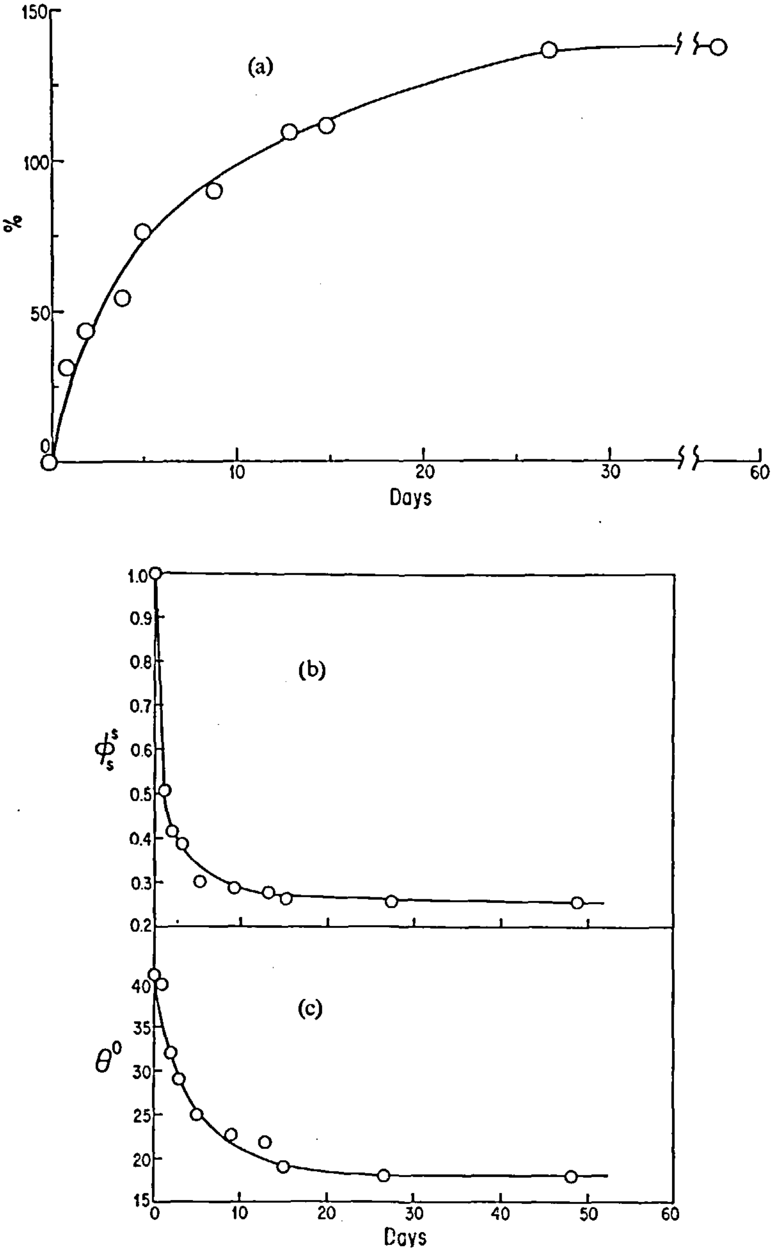

FIGURE 1 Polystyrene crosslinked with 5% DVB, polymerized in contact with mercury, swelled in $CH_2I_2$. (a) % increase in volume *vs* time. (b) Volume fraction of polymer in swelled polymer phase *vs* time. (c) Contact angle of $CH_2I_2$ *vs* time.

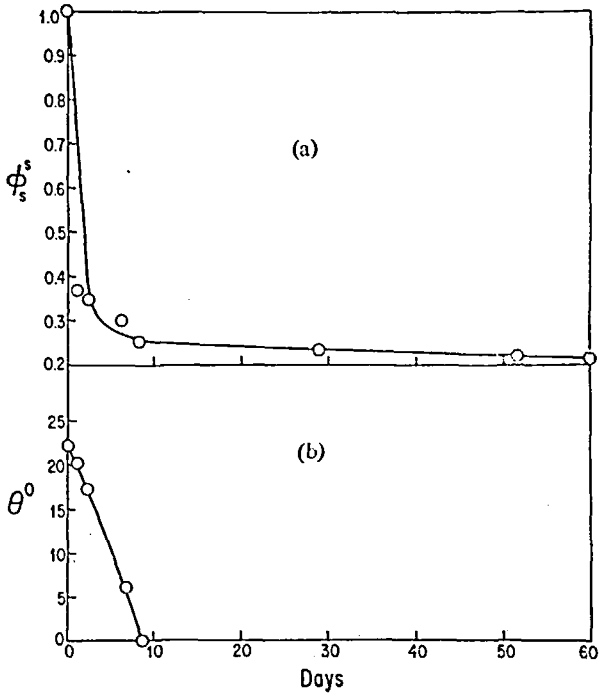

FIGURE 2 Polystyrene crosslinked with 5% DVB, polymerized in contact with mercury, swelled in α-bromonaphthalene. (a) Volume fraction of polymer in swelled polymer phase *vs* time. (b) Contact angle of α-bromonaphthalene *vs* time.

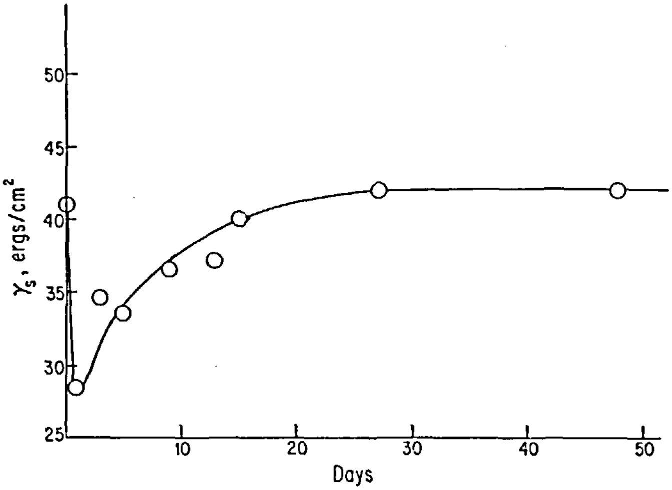

FIGURE 3 $\gamma_s$ of (unswelled) polystyrene (5% DVB) computed from contact angle data of $CH_2I_2$ on swelled polymer.

reproducibility of measurement deteriorated. No long-term results with $\alpha$-bromonaphthalene or aniline are shown in Table I, because Eq. (5) cannot be expected to be relevant when swelling has continued after $\theta$ has reached zero.

## DISCUSSION

The strong minimum in the computed value of $\gamma_s$, in the first few days of swelling (see Figure 3) was present with every sample. The most probable reason for this minimum is the fact that the bulk of the partly-swelled polymer was far below saturation. Hence there would be a gradient of chemical potential across the liquid–solid interface. The derivation leading to Eq. (5) would then be valid only as an approximation. $\gamma_{sl}$ would probably be greater than the value estimated using Eq. (3) and the relation derived in Ref. 6:

$$\gamma_{ab} = g_a + g_b - 2(g_a g_b)^{\frac{1}{2}} \tag{6}$$

So the contact angle would be larger than that corresponding to Eq. (4), for the composition of the swelled polymer.

The value of $\gamma_s$ computed by means of Eq. (5) is somewhat sensitive to errors in the measured values of $\theta$. For example, if $\theta \simeq 18°$ and $\gamma_l =$ 50.8 dynes/cm, a 1° error in $\theta$ causes approximately a 1 erg/cm$^2$ error in the computed $\gamma_s$. With the sessile drop-goniometer method, it is estimated[10] that the accuracy of most $\theta$ determinations (e.g., in the absence of nearly ideal conditions of measurement) is no better than ±3°, and precision is seldom better than ±2°.

The distribution of data, in Table I, is compatible with the above estimate of the precision of this kind of measurement. We may, accordingly, report that the surface free energy of unswelled polystyrene is in the range, 40 to 44 ergs/cm$^2$; the mid-value is 42 ergs/cm$^2$. The Ellison and Zisman result obtained with non-hydrogen bonding liquids was 43 ergs/cm$^2$, and Dann's result[11] was 42.5. The result of Good and Yu,[12] obtained by the modified Fox–Zisman method (i.e. plotting $\cos\theta$ *vs* $1/\sqrt{\gamma_l}$) and including both types of liquids, was 43 ergs/cm$^2$.

The present results reinforce the recommendation (see Ref. 4) that the unmodified Fox–Zisman method, of extrapolating data in graphs of $\cos\theta$ *vs* $\gamma_l$, should not be used when the extrapolation covers more than one or two dynes/cm in $\gamma_l$.

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