Surface-Chemical Criteria for Optimum Adhesion

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II. The Variability of Critical Surface Tension (γ_c) and its Choice

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According to Bikerman, who attributes failure in adhints to a weak boundary layer, it is almost impossible and meaningless to correlate adhesive strength to surface-chemical properties of adhints. Though his assertion seems to be confirmed by the recent studies of Schonhorn and his coworkers on the methods of CASING and TCR, not a few results have yet been accumulated, which show a close relation between them. In this paper surface-chemical criteria for the optimum adhesion are investigated and the minimum interfacial tension or the maximum wetting pressure is deduced from the published data and our own as a first approximation. It is emphasized that, when critical surface tension γ_c would be used as a measure of surface-chemical properties of solid, its variability according to liquid series (nonpolar, polar and hydrogen bonding liquids) should be carefully taken into consideration. The importance is shown for polyethylene and its fluorine substituted polymers, using newly measured contact angle data and Zisman's data. Results of Levine *et al.* and Schonhorn *et al.* on adhesive shear strength with epoxy adhesives are replotted against available values of γ_c obtained by the use of hydrogen bonding liquid (γ_c^e), which are thought to reflect wetting behaviors of epoxy adhesives quite well. Each curve shows a maximum around $\gamma_c^e = 40$ dyne/cm with few points falling off the curves.

INTRODUCTION

According to Bikerman[1], who attributes failure in adhints to a weak boundary layer, it is almost meaningless and impossible to correlate adhesive strength to surface-chemical properties of adhesives and adherends. Although his

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assertion seems to be confirmed by the recent studies of Schonhorn and his coworkers[2,3] on the methods of CASING and TCR, not a few experimental results have also been accumulated, which show a close relation between them. From these facts and general considerations on surface energetics, we concluded in a previous paper[4] that the optimum adhesion will be obtained at the condition minimizing interfacial tension γ_{SL} between adherends and adhesives. Using the Sell-Newmann relationship[5]

$$\gamma_{SL} = \frac{(\sqrt{\gamma_S} - \sqrt{\gamma_L})^2}{1 - 0.015\sqrt{\gamma_S\gamma_L}} \tag{1}$$

where γ_S and γ_L are surface tensions of the solid and liquid used, this condition will be realized at $\gamma_S = \gamma_L$, and is nearly consistent with a condition minimizing wetting pressure, $\gamma_L \cos \theta = \gamma_S - \gamma_{SL}$, for a given solid, where θ is contact angle. The conclusion is supported by various experimental results, including the study of Iyenger and Erickson[6] such that the optimum adhesion is obtained at the equal solubility parameters of both adherend and adhesive.

Since, however, there are many oppositions to the surface-chemical approach to adhesion, it is necessary to make clear the reason of contradiction as far as possible. One of the reasons is that we have no knowledge of surface tension of solid and interfacial tension between solid and liquid which are both required in the surface-chemical studies on adhesion. Instead, we often use Zisman's critical surface tension γ_c, as a measure of wetting properties of solid, and discuss its relation to adhesive strength. However, we must pay attention to the fact that values of γ_c as well as its physical meaning depend on the experimental conditions, especially on the choice of liquids used for contact angle measurements. Fowkes[7], and Good and Girifalco[8] have discussed the physical meaning of γ_c each from their own point of view. In this paper we would rather make it clear in relation to adhesion and discuss the optimum adhesion again.

VARIABILITY OF γ_c AND ITS MEANING

The fact that plots of $\cos \theta$ against γ_L for a solid surface give different straight lines, accordingly different values of γ_c, depending on liquid series used for contact angle measurements, had been pointed out by Fox and Zisman[9] for paraffin and n-hexatriacontane as early as in 1952. When measuring liquids are classified into three series, nonpolar liquids (A) such as n-alkane and di-n-alkylether, polar liquids (B) such as halogenated liquids and esters, and hydrogen-bonding liquids (C) such as water, glycerol

and formamide, and when γ_c's obtained by these liquid series are named $\gamma_c{}^A$, $\gamma_c{}^B$ and $\gamma_c{}^C$, we have $\gamma_c{}^A = 21$ dyne/cm, $\gamma_c{}^B = 12$ dyne/cm and $\gamma_c{}^C = 10$ dyne/cm for n-hexatriacontane. It is noteworthy that the nonpolar liquid series A gives a maximum value of γ_c and the hydrogen-bonding liquid series B gives a minimum for this nonpolar solid.

Dann[10] has recently tried to explain this fact combining the equations of Young, Fowkes and Good-Girifalco, but it can be understood more naturally and simily by considering the difference of interfacial tension as is done by Fox and Zisman. That is, from Young's equation

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} = \gamma_S - \gamma_{SL} - \pi \qquad (2)$$

putting $\gamma_{LV} = \gamma_c$ and $\gamma_{SL} = \gamma_{SL}{}^*$ at $\cos \theta = 1$, and assuming that $\pi = \gamma_S - \gamma_{SV}$ can be omitted, we obtain

$$\gamma_c = \gamma_S - \gamma_{SL}{}^* \qquad (3)$$

$\gamma_{SL}{}^*$ depends on the combination of solid and liquid; generally speaking, the combination of similar polarity will give a small value of $\gamma_{SL}{}^*$, accordingly a large value of γ_c for a given solid. In the case of paraffin, the liquid series of n-alkanes gives a large value of γ_c, 22 dyne/cm, while the polar liquid series gives a small value of 15 dyne/cm.

If the above consideration is valid, the liquid series of C is expected to give the smallest $\gamma_{SL}{}^*$ for hydrogen bonding solid and to give the maximum γ_c ($\gamma_c{}^C$). Let us refer to the studies of Zisman et al.[11] again. Nylon 6-6 gives $\gamma_c{}^C = 46.0$ dyne/cm with hydrogen-bonding liquids and $\gamma_c{}^B = 42.5$ dyne/cm with halogenated liquids, as expected. (Nonpolar liquids spread on nylon 6-6 and entirely wet it.) Similarly $\gamma_c{}^B$ might be maximum for solids of intermediate polarity. The instance has been given by Zisman et al.[11] in the same paper above referred to as $\gamma_c{}^B = 43.4$ dyne/cm and $\gamma_c{}^C = 32.8$ dyne/cm for polystyrene.

Variability of γ_c value had been noticed by Zisman himself in his earlier papers (9) (11) (12). Subsequently, however, he seems to have regarded the smallest value of γ_c's as the critical surface tension γ_c of the solid, until the recent studies on synthetic polypeptides[13], in which Zisman and his coworkers consciously utilize the difference of γ_c values for the conformational change of the samples. On the other hand, Sell and Neumann[5] have considered the extrapolated value of $\gamma_L \cos \theta$ to $\cos \theta = 1$, and named the largest value the critical wetting pressure β_c. Since β_c is equal to $\gamma_S - \gamma_{SL}{}^*$ according to Young's equation, it might vary with different liquid series like γ_c's, giving $\beta_c{}^A$, $\beta_c{}^B$ and $\beta_c{}^C$.

In order to make the above mentioned fact clearer and to fill the lack of necessary data, we carried out the contact angle measurements with three series of liquids, A, B and C, for polyethylene and its four fluorine-substituted

polymers[14]. Resulting values of $\gamma_c{}^A$, $\gamma_c{}^B$ and $\gamma_c{}^C$ are quite reasonable and as expected. The values will be used in this study, being listed in Tables I and II. An example of Zisman's plot is shown in Figure 1 for poly (trifluoroethylene)
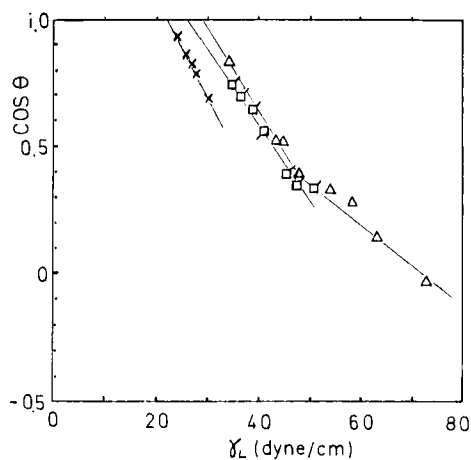

FIGURE 1   Zisman's plot for PVF₃.
× : A   Saturated hydrocarbons
□ : B   { □ : Halogenated liquids
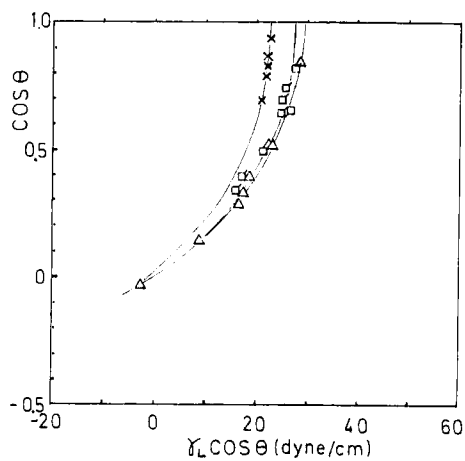   { ▫ : Esters
△ : C   Hydrogen liquids

FIGURE 2   Sell-Neumann's plot for PVF₃.
× : A   Saturated hydrocarbons
□ : B   { □ : Halogenated liquids
          { ▫ : Esters
△ : C   Hydrogen bonding liquids

(PVF$_3$), compared with Sell-Neumann's plot of the same data shown in Figure 2. γ_c^A, γ_c^B and γ_c^C agree fairly well with β_c^A, β_c^B and β_c^C respectively.

Eq. (3) shows that the maximum value of γ_c is closest to γ_S and is obtained with a liquid series which minimize γ_{SL}^*. The problem of what kind of liquid series minimizes γ_{SL}^* has been qualitatively discussed in the preceding paragraphs. The condition can be predicted a little more theoretically by the use of an extended Fowkes' equation proposed by us[15]. It is based on the following assumptions which are formally extended from Fowkes' equation.

$$\gamma_1 = \gamma_1^a + \gamma_1^b + \gamma_1^c, \qquad \gamma_2 = \gamma_2^a + \gamma_2^b + \gamma_2^c \qquad (4)$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^a\gamma_2^a} - 2\sqrt{\gamma_1^b\gamma_2^b} - 2\sqrt{\gamma_1^c\gamma_2^c} \qquad (5)$$

$$= (\sqrt{\gamma_1^a} - \sqrt{\gamma_2^a})^2 + (\sqrt{\gamma_1^b} - \sqrt{\gamma_2^b})^2 + (\sqrt{\gamma_1^c} - \sqrt{\gamma_2^c})^2 \qquad (5)'$$

where γ^a, γ^b and γ^c are components of surface tension γ, arising from dispersion force, polar (permanent and induced) force and hydrogen-bonding force respectively. γ^b and γ^c may be zero. Each parenthesis in Eq. (5)' is twice the difference between arithmetical and geometrical means, and therefore is negligibly small in the usual cases. Accordingly, when surface tensions of contacting materials both consist of the same kinds of components, in other words, in the cases of combinations of both nonpolar, both polar, and both hydrogen-bonding materials, their interfacial tension γ_{12} becomes negligibly small. In this case, measured γ_c becomes maximum and is nearly equal to γ_S. On the other hand, when γ_1, for instance, lacks one or two components, which are included in γ_2, the component might contribute predominantly to γ_{12}, and give a smaller value of γ_c.

Our extension of Fowkes' equation is merely formal, but has many advantages over the extended equation to two components proposed by Owens et al.[16] and Kaelble et al.[17]. It is useful particularly when we consider the wetting properties of solids for different liquid series A, B, and C, and when we want to estimate surface tension of solid. Surface tension of solid γ_S can be calculated by Eq. (5) and the relation $W_a = \gamma_1 + \gamma_2 - \gamma_{12} = \gamma_1$ $(1 + \cos\theta)$, using contact angle data of reference liquids, a part of which is listed in Tables I and II. (Details of the method are described in the paper (15).)

In Figure 3, calculated values of γ_S are compared with γ_c(max) and Zisman's γ_c for fluorine-substituted polyethylenes in their relation to fluorine percentage. As you can see, γ_S and γ_c(max) are nearly equal and go through the maximum at polyvinyl fluoride. Considering the change of polarity by fluorine substitution, this result is more reasonable than the linear decrease of Zisman's γ_c.
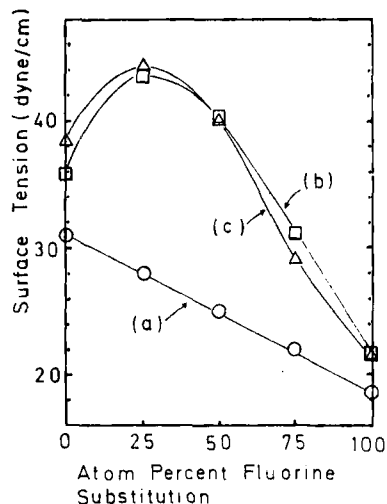
FIGURE 3   Zisman's γ_c, γ_c (max) and γ_S vs. fluorine percentage of fluorine-substituted polyethylenes.

(a) Zisman's γ_c
(b) γ_c (max)
(c) γ_S estimated by the extended Fowkes' equation

CHOICE OF CRITICAL SURFACE TENSION IN RELATION TO ADHESION

If it is true that γ_c has such a variability as above described, which γ_c should be chosen as the one related to adhesion? Now we consider the case that we measure adhesive strength of polymer solids of different surface-chemical properties to a given adhesive. A way is to take the maximum value of γ_c's as an approximate value of γ_S, and to correlate it or calculated value of γ_{SL}, for instance from Eq. (1), to adhesion. However Eq. (1) is neither theoretically grounded nor experimentally valid in a wide range of γ_S (or γ_L). Further, it can be shown that the maximum γ_c as well as the minimum or intermediate γ_c of solids have no significant relation with their wetting behaviors for a given adhesive, but the γ_c obtained with the same liquid series as the adhesive has a close relation with them. This fact is shown by the plot of cos θ against two kinds of γ_c (γ_c^C and Zisman's γ_c) of various polymers in Figure 4. Contact angles are measured with water, instead adhesives, for illustration. Such values of cos θ are closely related to γ_c^C obtained by the same series of hydrogen-bonding liquid as water, while Zisman's γ_c has almost no systematic relation to cos θ.

Now we are going to apply the above considerations to adhesion. In order to do so, we have to specify an adhesive and its liquid type. Here we consider
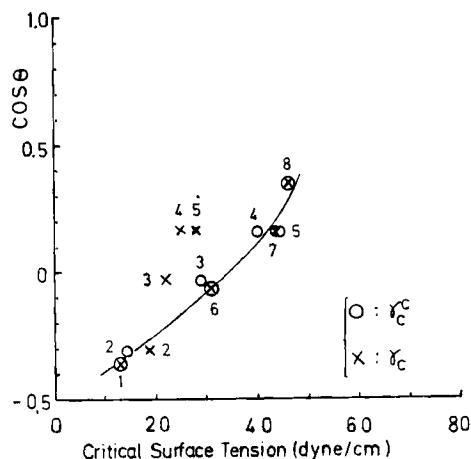
FIGURE 4 Plots of cos θ vs. Zisman's γ_c and $\gamma_c{}^C$.
1: Hexatriacontane, 2: PTFE, 3: PVF_3, 4: PVDF, 5: PVF, 6: PE, 7: PET, 8: Nylon 6.

epoxy adhesives for instance. Considering its chemical structure consisting of numerous hydroxy and amino groups, epoxy adhesives must be one of C type liquid of hydrogen-bonding character. Accordingly the wetting property of solids and adhesion for epoxy adhesives might be properly reflected by $\gamma_c{}^C$.

As for the relation of shear adhesive strength to γ_c for various polymers bonded by epoxy adhesives, there have been reported conflicting results in literatures. Levine et al.[18] have reported a linear relation between them while, on the contrary, Schonhorn et al. have given many examples showing that they bear no relation to each other. Which is correct? Here we try to reexamine these data according to our idea.

TABLE I
Tensile shear strength of adhesion by M. Levine et al.[18]

Films	T.S.S. (PSI)	Surface tension (dyne/cm)				
		γ_c	$\gamma_c{}^A$	$\gamma_c{}^B$	$\gamma_c{}^C$	γ_s
PET	2580	43	—	43.4	43.5	43.8
1,4 cyclohexylenedimethylene terephthalate	2600	43	—	—	—	—
PVDC	1900	40	—	44.0	40	45.8
PVC	1920	40	—	43.9	39	44.0
PVA	1650	37	—	36.3	—	—
PSt	1100	33	—	43.0	33	40.6
PVF	1320	28	—	43.2	44.2	43.5
PTFE	350	18.5	19.3	21.4	14.3	21.5

Note: T.S.S.: Tensile shear strength.

The results of Levine *et al.* and some surface-chemical data are listed in Table I. In Table II, all the results of Schonhorn *et al.* that we can evaluate

TABLE II

Tensile shear strength of adhesion by H. Schonhorn *et al.*

Substrates	T.S.S. (PSI)	Surface tension (dyne/cm)					Refer- ences
		γ_c	γ_c^A	γ_c^B	γ_c^C	γ_s	
PTFE	60	18.5	19.3	21.4	14.3	21.5	2(a)
PTFE/Gold	1570	40	—	—	47.0	—	3(c)
FEP Teflon	110	18.8	18.8	—	—	—	3(b)
FEP Teflon/Gold	2850	40.4	—	—	40.4	—	3(b)
PP	150	29	—	29.8	28.5	29.8	19
PVDF	2850	25	26.0	39.1	40.0	40.2	2(b)
PVF	580	28	—	43.2	44.2	43.5	2(b)
PE	500	31	—	38.3	30.9	35.6	2(b)
PE/Gold	2220	—	—	—	52.7	—	20
PE/Cr-80°-4min	2750	—	—	44.3	42.2	49.5	2(b)
Nylon 6 (Capran 77A)	610	46	—	43.4	46	46.5	3(b)
Nylon 6 (Capran 77A)	880	46	—	43.4	46	46.5	3(b)

Note: T.S.S.: Tensile shear strength.

for γ_c^C are gathered from their published papers. In the tables, γ_c represents Zisman's one. γ_c^A, γ_c^B and γ_c^C are obtained by replotting cos θ against γ_L of different liquid series, where the necessary data are taken from papers of Zisman *et al.*, Schonhorn *et al.* and ours. γ_S is calculated by our extended Fowkes' equation as aforementioned. As seen in the tables, the maximum value among γ_c^A, γ_c^B and γ_c^C agrees quite well with γ_S.

The shear adhesive strength in Tables I and II are all measured at room temperature, but the joint temperatures are different between two research groups. As it is 65.6°C (150°F) in the case of Levine *et al.*, data of Schonhorn
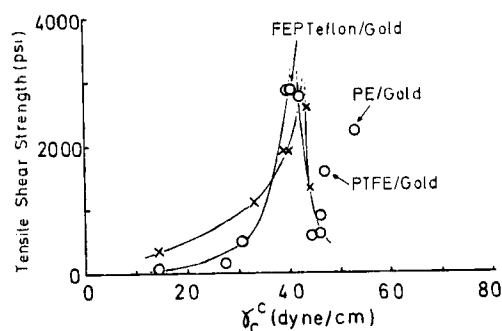

FIGURE 5   Relationship between tensile shear strength and γ_c^C of adherends.
○ : Schonhorn's data (jointed at 60°C)
× : Levine's data (jointed at 65°C)

et al. at 60°C nearest to that of Levine's are adopted for comparison. Figure 5 shows these values plotted against $\gamma_c{}^C$.

Notwithstanding that the experiments were done at quite different conditions independently, both curves have a surprisingly common feature in the point that the shear adhesive strength has a maximum around at $\gamma_c{}^C = 40 \sim 42$ dyne/cm.

It was reported that surface tension of adhesives used by Levine *et al.* is 50 dyne/cm, and that used by Schonhorn *et al.* was 33 dyne/cm. We cannot but accept them, however, considering difficulties of surface tension measurements of viscous adhesives, the difference might be less. It is interesting that the value of 40 ~ 42 dyne/cm is about the mean of both surface tensions.

If it may be accepted for the optimum adhesion to occur at the minimum interfacial tension, $\gamma_c{}^C$ at the maximum adhesion should be the largest among γ_c's of the solid, and therefore nearly equal to γ_S, as discussed before. If surface tension of epoxy adhesives could be assumed to be 40 dyne (strictly speaking, 42 dyne/cm in the case of Levine *et al.*), the results in Figure 5 would be consistently explained by the criterion $\gamma_S = \gamma_L$ for the optimum adhesion.

In Figure 5 a few points lie off the curves. These surfaces are all formed on gold foil and show large $\gamma_c{}^C$, particularly $\gamma_c{}^C = 52.7$ dyne/cm for polyethylene/gold. Schonhorn and Ryan have explained this fact by the increase of density due to the formation of trans-crystalline region (TCR). TCR also causes the increase of adhesive strength by eliminating the weak boundary layer. Surface properties may be naturally affected by the change of structure, however the values of $\gamma_c{}^C$ above referred seem to be too high.

The results of Schonhorn *et al.* on CASING are not referred to in this paper, because contact angle data to give $\gamma_c{}^C$ are not known in detail. They found that very high joint strength was obtained by CASING, in spite of the fact that surface tension remained unchanged or decreased. In this case, however, it is interesting to see what results can be obtained by the measurements of all $\gamma_c{}^A$, $\gamma_c{}^B$ and $\gamma_c{}^C$. As shown in Table II, $\gamma_c{}^B$ and $\gamma_c{}^C$ of polyvinylidene fluoride (PVDF) are rather high (39.1 dyne/cm, 40.0 dyne/cm), though its $\gamma_c{}^A$ and Zisman's γ_c are low (26.0 dyne/cm, 25 dyne/cm).

In conclusion, setting aside the detailed relation, it can be said that adhesive strength has a close relation with some surface-chemical functions of adhesives and adherends, if they are carefully chosen.

References

1. J. J. Bikerman, *The Science of Adhesive Joints* (Academic Press, N.Y., 1968), 2nd ed., p. 137.
2. H. Schonhorn and R. H. Hansen, (a) *Polymer Letters* **4**, 203 (1966), (b) *J. Appl. Polym. Sci.* **11**, 1461 (1967), (c) ibid. **12**, 1231 (1968).

3.   H. Schonhorn and F. W. Ryan, (a) *J. Polym. Sci.*, *A-2* 6, 231 (1968), (b) ibid. 7, 105 (1969), (c) *J. Adhesion* 1, 43 (1969).
4.   T. Hata and Y. Kitazaki, *Nihon Setchaku Kyokaishi* (*J. Adhesion Soc. Japan*) 7, 224 (1971).
5.   D. Drieger, A. W. Neumann and P. J. Sell, *Kolloid Z. u. Z. Polymere* 201, 52 (1965), 204, 101 (1965), P. J. Sell and A. W. Neumann, *Angew. Chem.* 78, 321 (1966).
6.   Y. Iyengar and D. E. Erickson, *J. Appl. Polym. Sci.* 11, 2311 (1967).
7.   F. M. Fowkes, *Ind. Eng. Chem.* 56, 40 (1964).
8.   R. J. Good and L. A. Girifalco, *J. Phys. Chem.* 64, 561 (1960).
9.   H. W. Fox and W. A. Zisman, *J. Colloid Sci.* 7, 428 (1952).
10. J. R. Dann, *J. Colloid Sci.* 32, 302 (1970).
11. A. H. Ellison and W. A. Zisman, *J. Phys. Chem.* 58, 503 (1954).
12. H. W. Fox and W. A. Zisman, *J. Colloid Sci.* 5, 514 (1950).
13. R. E. Baier and W. A. Zisman, *Macromolecules* 3, 70 (1970).
14. Y. Kitazaki and T. Hata, *Nihon Setchaku Kyokaishi* (*J. Adhesion Soc. Japan*), in press.
15. T. Hata, *Kôbunshi* (*High Polymers, Japan*) 17, 594 (1968), Y. Kitazaki and T. Hata, *Nihon Setchaku Kyokaishi* (*J. Adhesion Soc. Japan*), in press.
16. D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.* 13, 1711 (1969).
17. D. H. Kaelble and K. C. Uy, *J. Adhesion* 2, 50 (1970).
18. M. Levine, G. Ilkka and P. Weiss, *Polymer Letters* 2, 915 (1964).
19. H. Schonhorn, F. W. Ryan and R. H. Hansen, *J. Adhesion* 2, 93 (1970).
20. H. Schonhorn and F. W. Ryan, *Advances in Chemistry Series*, 87 (Am. Chem. Soc., Washington, 1968), p. 140.