Solubility of Hydrogen in Polyethylene by a Semimicro Method

Thomas M. Deas, Jr., Hans H. Hofer, and Malcolm Dole*

Department of Chemistry, Baylor University,
Waco, Texas 76703. *Received November 8, 1971*

ABSTRACT: A new semimicro method for the determination of the solubility of hydrogen in 0.5-g or smaller samples of polyethylene is described. The method is based on the use of a gas chromatograph with special types of sample loops. In agreement with previous findings of Michaels and Barrer on other gases, the solubility was found to be a linear function of the amorphous fraction. This was not true, however, for irradiated polyethylene or for a sample of polyethylene containing extended-chain crystals.

In this paper a new method for the determination of the solubility of hydrogen in linear polyethylene (PE) is described. Whereas Michaels and Parker[1] required 150 g of sample and Ash, *et al.*,[2] 20 g in their techniques, our method gives satisfactory results with only 0.5 g or less of sample. In neither of the important investigations of Michaels, *et al.*,[1,3] or Ash, *et al.*,[2] was linear PE investigated. We also give below provisional data for the solubility of H_2 in irradiated linear PE and in a sample of extended- chain high-density PE.

Experimental Section

(A) Materials. Unless otherwise stated all of the PE samples were prepared from Marlex-6002 film. Table I lists their densities, weights, and approximate thicknesses. Sample 1 was the film as received. Samples 2 and 3 were cylindrical samples formed by melting the PE in a glass tube under nitrogen and cooling to room temperature. Sample 4 consisted of several sheets of the film pressed together and melted between glass plates and then cooled to room temperature. Samples 5 and 6 were the same as 4 except they were rapidly cooled with cold water. Samples 7 and 8 were similarly prepared except that they were cooled slowly from 180° to room temperature. Sample 9 was a sample of PE crystallized at 226° and 4700 atm by Professor B. Wunderlich[4] in 1963. The density and crystallinity values were supplied by him. Sample 10 was PE γ irradiated to a dose of 22.2 Mrads *in vacuo* at room temperature and then immediately exposed to the air. Sample 11 was prepared by pressing several layers of film between glass plates, heating to the melting range, and then quenching in ice water. Sample 12 was sample 11 irradiated to 13.2 Mrads, annealed at 150° until clear, and quenched in ice water. The resulting γ-irradiated sample was much clearer than the original sample before irradiation. It is well known[5] that irradiation of PE inhibits crystallization on cooling from the melt but does not materially affect the crystallinity if irradiated at room temperature without further heat treatment (as was the case with sample 10).

The weight fraction of amorphous content, α_w, was calculated from the equation

$$\alpha_w = 5.814v - 5.831 \text{ at } 30° \qquad (1)$$

where v is the specific volume of the sample. The numerical factors were calculated taking the specific volumes of the 100% crystalline and amorphous fractions equal to 1.003 and 1.175 $cm^3\ g^{-1}$, respectively, as estimated at 30° from the values used by Michaels and Bixler[3] at 25°. The density data of Table I were determined at 30° in a density gradient column.

The gases used were Linde hydrogen, listed at 99.5% purity, and CP grade Matheson deuterium, listed at 99.5% (atom) minimum.

(B) Sample Loop and Vacuum System. A vacuum system was constructed so that the Pyrex glass loop containing the sample could be either evacuated and filled with hydrogen at a specified pressure or purged of hydrogen by means of a rapid blast of nitrogen gas. The glass loop is illustrated in Figure 1 and was attached to the vacuum line by means of rubber tubing on the glass tubes at the left of the drawing. The PE sample was placed in the loop just to the right of the ball joint on the lower half of the detachable U tube.

After evacuation, hydrogen was admitted to the sample loop and pressure adjusted so that later when the sample loop was removed from the vacuum line and immersed in a constant-temperature bath, the pressure was exactly 1 atm at the selected temperature. One experiment was done at 0.5 atm to test Henry's law.

After solubility equilibrium had been attained after 24 hr or more, the ambient hydrogen was swept out of the sample loop by the blast of nitrogen described above, and then the loop was removed from the constant-temperature bath; after a resting period of 24 hr the loop was connected to the gas chromatograph (gc) input system. The special gas inject system for the gc included a Varian Aerograph nut-type six-port gas sample valve which made it possible to sweep the hydrogen which had diffused out of the sample into the gc.

Inasmuch as the gc measured moles of hydrogen directly, after calibration, it was unnecessary to know the volume of the sample loops. However, the volume of one loop, 2.4 ml, was determined in order to use it in measuring out the moles of hydrogen or deuterium necessary to calibrate the gas chromatograph.

(C) The Gas Chromatograph. The gc was a Labline Chromalyzer 100 gas chromatograph containing a column packed with 13A molecular sieve and held at 152°. It was found necessary to replace the matched 40-ohm tungsten filaments in the thermal conductivity bridge about once every 6 months in order to reduce the noise and restore the sensitivity to normal. The detectors were obtained from the Burell Corp. of Pittsburgh, Pa. Calibration curves were linear, extrapolating to zero response at 0 mol of H_2 gas. The slopes of the lines were 1.68×10^{-9} mol of H_2 and 2.72×10^{-9} mol of D_2 per unit area, calculated at the same bridge current in each case. Oxygen, indicative of a vacuum leak, showed up as a shoulder on the hydrogen peak. Nitrogen was the carrier gas. The area of the gc signal on the recorder was calculated by multiplying the height by the width at half-height.

After the first injection of hydrogen into the gc, the sample was allowed to stand again for another period of about 12 hr before a second injection. It was found that the amount of hydrogen that could be detected on a third injection was the order of magnitude of the experimental uncertainty (see Table II), so that a third injection was abandoned. The amount of hydrogen injected into the gc on the second injection varied from 3% to less than 1% of that of the first injection.

(D) Corrections for Residual Ambient Hydrogen. One of the greatest difficulties in solubility coefficient measurements by the equilibrium method is to remove all ambient hydrogen from the gas

---

[1] A. S. Michaels and R. B. Parker, Jr., *J. Phys. Chem.*, **62**, 1604 (1958).

[2] R. Ash, R. M. Barrer, and D. C. Palmer, *Polymer*, **11**, 421 (1970).

[3] A. S. Michaels and J. H. Bixler, *J. Polym. Sci.*, **50**, 393 (1961).

[4] B. Wunderlich and T. Arakawa, *ibid.*, *Part A*, **2**, 3697 (1964).

[5] T. F. Williams, H. Matsuo, and M. Dole, *J. Amer. Chem. Soc.*, **80**, 2595 (1958).

Table I
Properties of Polyethylene Samples Studied

Sample no.	Density, g ml^{-1}, at 30°	Weight, g	Thickness (l), cm
	H_2 Experiments		
1	0.9570	0.2201	0.025
2	0.9684	0.1930	0.370
3	0.9661	0.3700	0.570
4	0.9564	0.5471	0.175
5	0.9502	0.3927	0.090
6	0.9491	0.5392	0.121
7	0.9711	0.6664	0.480
8	0.9667	0.2890	0.195
9[a]	0.9938 (25°)	0.2128	0.1
10[b]	0.9523	0.4955	0.121
11	0.9490	0.4725	0.240
12[c]	0.9322	0.7135	0.240
	D_2 Experiments		
3	0.9661	0.3696	0.570
4	0.9564	0.7029	0.175
7	0.9711	0.6397	0.48

[a] Extended chain. [b] Sample 6 irradiated to 22.2 Mrads. [c] Sample 11 irradiated to 13.2 Mrads.

Table II
Experimental Data for a Typical Experiment.
Sample 3 at 25°[a]

t_1, hr	24	t_4, hr	12	σ	0.637
t_2, sec	5	A_2	2.53	σ_{corr}	0.645
M_t/M_∞	0.012	t_5, hr	12		
t_3, hr	24	A_3	1.70	α_w	0.186
A_1	76.08	A_4	10.0	σ_a	3.47

[a] Solubility data in grams of H_2 per 100 g of PE × 10^4 at 1 atm of pressure; 0.3700 g of PE, l = 5.70 mm. t_1 = H_2 sample equilibration time, t_2 = flushing time, t_3 = time between flushing and first injection, t_4 = time between first and second injections, t_5 = time between second and third injections, A_1 = chromatogram area on first injection (area units in millimeters × centimeters), A_2 = chromatogram area on second injection, A_3 = chromatogram area on third injection, A_4 = chromatogram area equivalent to dead space hydrogen—to be subtracted from the total of $A_1 + A_2 + A_3$, σ = solubility coefficient as measured from $A_1 + A_2 + A_3 - A_4$, σ_{corr} = solubility coefficient after correcting for diffusive loss of hydrogen, σ_a = corrected solubility coefficient divided by weight fraction α_w of amorphous content to yield solubility of hydrogen in 100% amorphous PE.

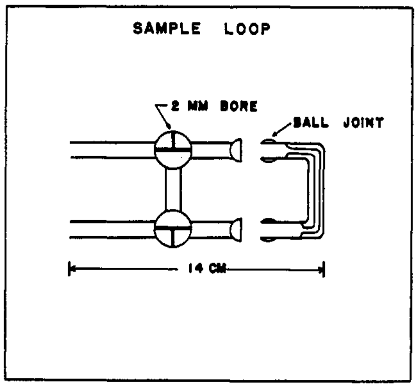

Figure 1. View of sample loop (rotate through 90° for actual operating position).

space about the sample without leaving any residual ambient hydrogen in the loop, which would later be included as part of the dissolved hydrogen, and at the same time preventing as far as possible diffusion of dissolved hydrogen out of the sample. In our work we used a 5-sec flush; that is, after hydrogen solubility equilibrium was attained, both valves of the sample loop (Figure 1) were opened for 5 sec. During this 5 sec flush nitrogen at 1.2 atm of pressure expanded out of a N_2 ballast bulb, through the sample loop, sweeping the hydrogen before it into 2- and 5-l. vacuum ballast bulbs. The rotary pump at the same time was pumping on the system.

To test the efficiency of ambient hydrogen removal by this method, a solid glass sample of approximately the same dimensions as the PE samples was inserted into a sample loop and the loop was filled with hydrogen at 1 atm of pressure and then given the 5-sec flush. After the 5-sec flush, the residual hydrogen left in the sample loop was swept into the gc by means of nitrogen and the amount of hydrogen was determined. For PE samples weighing 0.5 g, the correction for the residual hydrogen was about 10% of the total dissolved hydrogen (at 1 atm of pressure). The residual hydrogen correction varied somewhat from loop to loop, with the shape of the sample and with the amount of grease on the stopcocks. In general, the correction could be determined to ±5% so that the net uncertainty in the solubility coefficient was 5% of 10% or about 0.5%.

(E) Corrections for Diffusive Loss of Dissolved Hydrogen. During the flushing period, some of the hydrogen diffuses out of the PE, and this loss must be corrected for. Following the nomenclature of Ash, *et al.*,[2] let M_t/M_∞ be the fraction of the hydrogen dissolved in the PE which diffuses out during the flushing time t. According to diffusion theory, the diffusion out of the polymer can be expressed by the following equation, valid for values of M_t/M_∞ up to 50%[6] (if D is constant with time)

$$M_t/M_\infty = 4(Dt/\pi l^2)^{1/2} \qquad (2)$$

where D is the diffusion coefficient in square centimeters per second, t is the time in seconds, and l is the thickness of the sheet in centimeters. Rearranging eq 2

$$(M_\infty - M_t) = M_\infty - 4M(Dt/\pi l^2)^{1/2} \qquad (3)$$

The left-hand side of eq 3 is the moles of hydrogen dissolved in the PE minus that lost during flushing and is equal to σ after multiplication by a factor which converts the measured $M_\infty - M_t$ to grams of H_2 per 100 grams of PE. Hence, knowing M_∞ at zero time and the slope of the lines of Figure 2, the diffusion coefficient, D, can be calculated. These calculations will be discussed below.

Equation 3 also predicts that the thicker the sample the less the relative loss of the dissolved hydrogen during the flushing period. This prediction is verified by the data of Figure 2, where the much smaller slope of the line representing the data of the thick sample can be seen.

Data for a typical experiment are given in Table II, where the finally calculated σ_a value represents the grams of hydrogen dissolved at 1 atm of pressure in 100 g of a hypothetical 100% amorphous polymer.

In most of our experiments the dissolved hydrogen was measured only after a 5-sec flush. In this case, M_t/M_∞ of eq 2 was calculated knowing D and t, and the resulting ratio was used to convert σ to σ_{corr} by dividing σ by $1 - (M_t/M_\infty)$. The diffusion coefficients at different temperatures used in our calculations were estimated from the values for branched PE at 0.56 volume fraction of amorphous polymer given by Ash, *et al.*,[2] by multiplying the latter values at each selected temperature by the ratio $\alpha_w/0.56$. The values of D for deuterium were assumed to be equal to the values for hydrogen after division of the latter by $\sqrt{2}$.

Data and Discussion

All of the measured solubility values in units of grams of H_2 per 100 g of PE are collected in Table III. With the exception of

---

[6] J. Crank and G. S. Park, "Diffusion in Polymers," Academic Press, New York, N. Y., 1968, p 16.

TABLE III
SOLUBILITY DATA FOR HYDROGEN IN POLYETHYLENE[a]

Sample no.	α_w[b]	M_t/M_∞	$D \times 10^6$, cm² sec⁻¹	$\sigma_{corr} \times 10^4$ g of H_2/100 g of PE	$\sigma_a \times 10^4$
		0°			
6		0.031	0.8	0.813	2.74
		25°			
1	0.245	0.239	1.89	0.783	3.20
2	0.175	0.017	1.35	0.576	3.29
3	0.186	0.012	1.47	0.645	3.47
4	0.250	0.044	1.92	0.803	3.21
5	0.285	0.093	2.22	0.948	3.33
6	0.297	0.069	2.27	0.951	3.20
7	0.157	0.012	1.22	0.548	3.49
8	0.181	0.034	1.44	0.646	3.57
9	0.031	0.026	0.15	0.559	18.3
10	0.274	0.067	2.12	1.09	3.97
11	0.297	0.035	2.28	1.31	4.41
12	0.407	0.040	3.07	1.50	3.68
		35.5°			
2		0.020	2.4	0.645	3.69
4		0.053	3.4	0.900	3.60
6		0.087	4.4	1.02	3.43
9		0.033	0.38	0.580	19.0
10		0.083	4.4	1.33	4.84
		45.5°			
3		0.016	3.8	0.735	3.95
5		0.134	5.7	1.090	3.82
6		0.101	5.9	1.097	3.69
9		0.038	0.58	0.598	19.5
		D_2 Solubility			
				g of D_2/100 g of PE	
		25°			
3		0.010	1.05	1.44	7.74
4		0.037	1.36	1.90	7.59
7		0.011	0.87	1.34	8.53
		35.5°			
3		0.013	1.85	1.65	8.87

[a] Grams of gas per 100 g of PE at 1 atm of pressure. [b] α_w was taken to be the same at 0, 35.5, and 45.5° as at 25°.

the data for sample 6 at 0°, sample 7 (D_2 experiment) at 25°, sample 10 at 35.5°, and sample 3 and sample 9 at 45.5°, all of the σ_{corr} values are averages of two or more experiments. The σ_a values are σ_{corr}/α_w, or the solubility of hydrogen in grams calculated for 100 grams of 100% amorphous polymer. All of these values should be equal if the hydrogen dissolves only in the amorphous fraction and if the nature of the amorphous fraction is independent of the degree of crystallinity. The latter postulate can be tested by plotting σ_{corr} as a function of α_w. This is done in Figure 3, where it can be seen, in agreement with the previous observations of Michaels[1,3] on many gases (but not hydrogen) that there is a linear relation between the solubility and amorphous content. Hence the accuracy of the data can be judged by comparing the values of σ_a of Table III (omitting data for samples 9–12 inclusive). The average deviation for the data at 25° from the mean value of 3.35×10^{-4} is 0.13×10^{-4} or 3.9%. In the case of repetitive experiments, the reproducibility of the data was obtained to within ±1% and for the larger samples to ±0.5%.

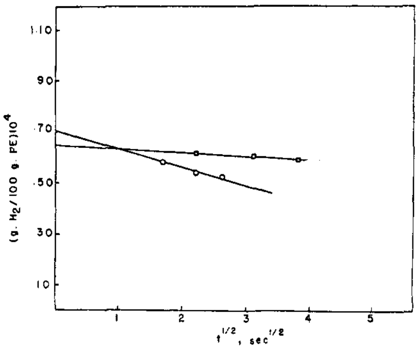

Figure 2. Measured solubility of hydrogen as a function of the square root of the flushing time: (○) sample 1, (□) sample 8.

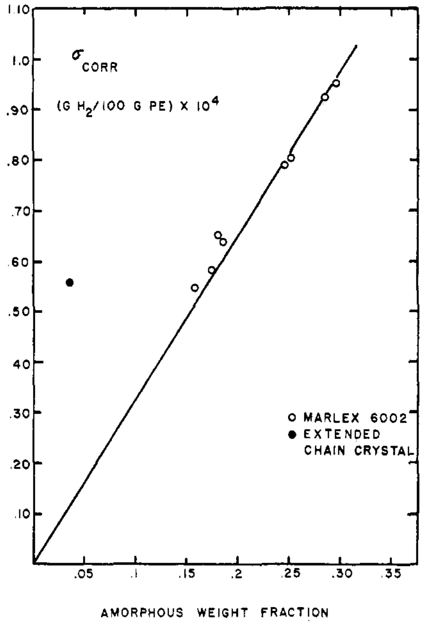

Figure 3. Hydrogen solubility at 1 atm pressure of samples 1–9 at 25° plotted as a function of the amorphous weight fraction.

As mentioned above, the M_t/M_∞ ratios of Table III are the fractions of hydrogen believed to have diffused out of the sample during the 5-sec flushing period. These values are all less than 10% except for the film, sample 1, and for samples 5 and 6 at 45.5°. In the case of sample 5 at 45.5° with an M_t/M_∞ value of 0.134, the uncertainty in σ_{corr} due to this correction factor would be only about 0.7% even if D were in error by 15% because M_t is proportional to $D^{1/2}$.

The M_t/M_∞ ratio for the film sample, sample 1, is very large, 0.239. This means that 24% of the hydrogen diffused out of the thin film during a flushing period of only 3 sec. It will be noticed from Figure 2 that the ordinate of the straight line extrapolated to zero time for the film sample, sample 1, namely, 0.704×10^{-4} g of H_2/100 g of PE, is considerably less than the value of σ_{corr} for sample 1, or 0.783×10^{-4}, given in Table III. The value in Table III was obtained by correcting σ_{measd} for the 3-sec flush time by dividing it by $(1 - M_t/M_\infty)$ as explained above. Here M_t/M_∞ was calculated from eq 3 using a value of D equal to 1.9×10^{-6} cm² sec⁻¹, as estimated from the data of Ash, *et al.*[2] If the diffusion coefficient is calculated from the slope and intercept of the sample 1 curve of Figure 2, the low value of 1.25×10^{-6} cm² sec⁻¹ is obtained. This low value is due either to a different type of diffusion in the partially oriented film or to a marked change of D with concentration which would make most uncertain the extrapolation of Figure 2.

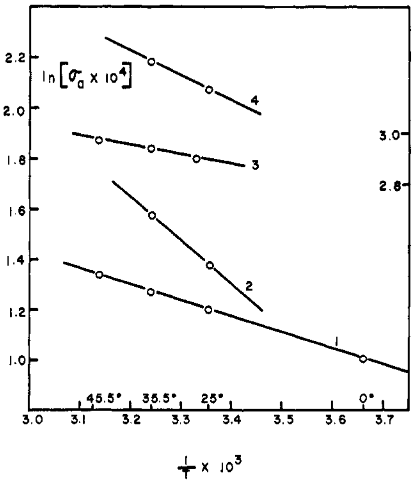

Figure 4. Logarithm of solubility in 100% amorphous polymer as a function of reciprocal temperature: curve 1, bulk polyethylene; curve 2, irradiated polyethylene; curve 3, extended-chain crystals; curve 4, deuterium in bulk polyethylene; right-hand scale for curve 3.

It is interesting to compare our mean value at 25° of 3.35×10^{-4} g of H_2/100 g of PE with the value calculated by Ash, *et al.*,[2] 0.034 cm^3 of H_2 at STP/cm^3 of PE at 1 atm of pressure for 100% amorphous polyethylene. Taking the density of the latter[3] to be 0.854, the result of Ash, *et al.*,[2] is 3.58×10^{-4} g of H_2/100 g of amorphous PE. This value is about 6% higher than ours. The polyethylene used by Ash, *et al.*,[2] was apparently a low-density, branched PE.

The heats of solution of hydrogen and deuterium as calculated from the slopes of the $\ln \sigma_a$ *vs.* $1/T$ plot of Figure 4 are 1.3 and 1.9 kcal mol^{-1}, respectively. In the previous work,[2] Ash, *et al.*, found 2.2 kcal mol^{-1} for hydrogen in their PE. All of these heats are endothermic which means that the hydrogen or deuterium gas solubility rises with temperature.

The data of Ash, *et al.*,[2] agreed with Henry's law over the pressure range 0–250 Torr. We made one measurement at 0.465 atm of pressure in the case of sample 5 at 25° and obtained a value of 0.464×10^{-4} g of H_2 per 100 g of PE, as compared to 0.433×10^{-4} and 0.449×10^{-4} for two experiments using sample 5 at 1 atm corrected to a pressure of 0.465 atm. Thus, within the limits of experimental uncertainty, Henry's law appears to be valid up to 1 atm.

Especially interesting are the data obtained in the case of the extended-chain and highly crystalline sample 9 of Table I. These data were unusually high when reduced to 100% amorphous content. Furthermore, the change in solubility with temperature was small (see Figure 4) and resulted in a heat of solution of only 0.6 kcal mol^{-1}. If these results on this one sample are correct, we have to conclude that the mechanism of solution of hydrogen in the extended-chain sample is different from that in ordinary bulk polyethylene.

Equally interesting is the effect of irradiation on the hydrogen solubility in PE. Sample 10 was sample 6 irradiated to a dose of 22.2 Mrads and then exposed to air before making the solubility measurements. There may have been some postirradiation oxidation of the sample but not enough, we believe, to affect the solubility materially. If the PE is given a postirradiation annealing to eliminate trapped free radicals and thus to prevent postirradiation oxidation, the crystallinity is drastically diminished and the density reduced to 0.932; see sample 12 irradiated to 13.2 Mrads, Table I. Both of the irradiated samples show an increase in σ_a, with the increase of sample 10 being greater than that of sample 12, as would be expected because of almost double the irradiation. If the temperature of the sample is maintained at room temperature, the irradiation produces no significant changes in the crystallinity at these relatively low doses.[5] Hence the solubility increase cannot be explained in terms of increased amorphous content of the sample. Probably the irradiation produces defects in the solid such as branch points (cross-links) and unsaturated groups. As the irradiation proceeds, hydrogen is evolved in the crystalline as well as in the amorphous region and has to force its way out of the solid. This action of the hydrogen may produce fissures or channels in the PE which would promote the solubility of the hydrogen. The increase in the endothermic heat of solution on irradiation from 1.3 to 3.4 kcal mol^{-1} (see Figure 4) may be the result of cross-linking in the amorphous regions which would restrict the molecular motions necessary for solution of the hydrogen to occur.

Acknowledgments. This research was supported by income from the chair in chemistry at Baylor University endowed by a gift from The Robert A. Welch Foundation. Dr. J. A. Reid of the Phillips Petroleum Company kindly supplied the Marlex-6002 polyethylene and Professor B. Wunderlich of Rensselaer Polytechnic Institute the sample of high-pressure crystallized polyethylene.