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MASTER

Ballentine and Manowitz (1) made the original observation that monomers adsorbed on carbon black surfaces could be polymerized by radiation. In their experiment some days elapsed between adsorption of the monomer, which was butadiene, and irradiation. There was another significant time lapse between irradiation and the performance of the experiment giving evidence of polymerization. The authors recognized that they did not know how much polymerization had occurred before radiation. Post-polymerization is a well known phenomenon in the radiation chemistry of monomers. Thus both prepolymerization and post-polymerization were possible in their experiment. Walker (2) reports that irradiation at energy levels greater than 50 e.v. introduces changes in the structure of carbon. Ballentine and Manowitz used 200,000 rep/hr. of γ -irradiation for 5-12 hours, which undoubtedly increased the number of defects in the carbon black.

In fact, the sequence of events that must be considered in radiation experiments with monomers adsorbed on carbon black is relatively complex (Table I). Here we recognize the possibilities that radiation affects both monomer and adsorbate, that either defects in the adsorbate or radiation can initiate polymerization, that monomer can polymerize rapidly or with an induction period such that substantial polymerization requires many hours ("post-polymerization"), and that the monomer source may be adsorbed molecules or "free" molecules (i.e., molecules in the

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vapor space that are in equilibrium with the adsorbed molecules).

Subsequent studies of adsorption polymerization have been carried out with clay or similar materials as the adsorbate (see for example Blumstein (3)). More recently, Strelko and Vysotskii (4) observed the polymerization of thiophene on silica gel. In our laboratories we have paid particular attention to disc-shaped molecules such as thiophene as adsorbents. With furan as the adsorbed monomer and the well-characterized carbon black Graphon as adsorbate (5) we observed a definite effect of the thickness of the adsorbed layer on the nature of the polymerization (6).

Experimental Methods

Physical adsorption is by definition a readily reversible process. If the pressure of the gaseous adsorbate is increased, then decreased on the original value, a plot of adsorbent weight as a function of time should increase, then decrease to the original value. Any hysteresis is ascribed to capillary condensation, chemisorption, or (in the case that monomers are the adsorbates) polymerization.

A sensitive method for measuring weight as a function of time for an adsorbent in a vacuum system is the essential requirement for studies of polymerization of adsorbed monomers. Since the weight adsorbed under any given conditions of gas pressure and adsorbent temperature is directly proportional to the specific surface of the adsorbent, the sensitivity can be enhanced by choosing a high-surface adsorbent. Graphon is a non-porous carbon black with a specific surface of 85 sq. m./g. Interparticle condensation which can lead to hysteresis, is not significant unless adsorption has proceeded well past the monolayer point (7).

With Graphon as the adsorbent, a silica spring with a sensitivity of 10 mg./mm. has given meaningful results in our experiments. However, the Cahn electro-

balance, used with a setting that gives one division on the recorder paper for 10 micrograms, has given us excellent weight-time charts without serious noise problems.

In either case, the basic experiment in our laboratories consists of the following steps:

1. With 10-1000 mg. Graphon loaded onto spring or balance, heat the portion of the vacuum line containing the sample to 250°C . for four hours, meanwhile pumping down the vacuum line at pressures below one micron.
2. Equilibrate the Graphon at room temperature ($25-27^{\circ}\text{C}$.).
3. Isolate the vacuum system from the vacuum pump and open a Teflon stopcock to expose the Graphon to vapors in equilibrium with a liquefied sample of the adsorbate maintained at a predetermined temperature of the order of -20°C . The quantity of liquid is sufficient so that it does not all evaporate during adsorption.
4. Follow adsorption as a function of time for a period of 1-24 hours.
5. Close the stopcock between the liquefied adsorbate and the adsorbent.
6. Open the stopcock between the system and the vacuum pump and pump down the system; follow desorption as a function of time for a period of 1-24 hours.

Radiation experiments are carried out by going through the same process, but with the adsorbent lying free in a container. Weighing is not necessary if the conditions in each step are the same as those that have been used in a previous experiment with the adsorbent on a spring or balance. Within minutes after step 5 is taken, the sealed system containing the adsorbent and its adsorbate is placed in a beam of 6 m. e. v. electrons and irradiated with 100,000 rads. This is done at room temperature. A side-arm on the glass system is then cooled with solid carbon dioxide and the amount of adsorbate desorbed and condensed in the side-arm is measured

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volumetrically.

Results:

Exposure of furan vapors to Graphon under conditions that form less than a monolayer results in physical adsorption initially. With time an irreversible process, apparently polymerization, becomes significant even if there is no radiation step. This statement is based on a number of experiments, of which the most significant are summarized in Table 2. The material that remained after desorption was investigated in previous work with polyfuran resulting from radiation of Graphon with adsorbed furan (6). It should be noted that adsorption in itself is a fairly rapid process, being complete within about 30 minutes (5).

One characteristic of these experiments was the variation from run to run in the amount of irreversible adsorption. This was observed for adsorption at 25°C. and at -18°C. In fact, at -18°C. we were not able to get repeatable results in our attempts to measure adsorption isotherms (Fig. 1). These results resemble those obtained in free-radical polymerization of bulk monomers, in which case the variable induction period gives considerable variation in the amount polymerized at a given polymerization time.

With this background, it is possible to consider the effect of the time pattern on the results obtained on irradiation of the Graphon with furan adsorbed on it (Table III). All of our experimental results fall into a pattern in which a rapid polymerization initiated by high energy electrons is superimposed on a slow polymerization that is possibly initiated by defects in the Graphon. (It should be noted that Ballentine and Manowitz (1) reported that Statex 125, the carbon black that they used, reacted with butadiene on standing, even if there was no irradiation. On the other hand, Graphon did not fix any butadiene in their experiments, even when they used a γ -ray dosage of 200,000 rep/hr. for 12 hours).

Other monomers should be considered before any generalizations are offered. 1,4-Cyclohexadiene on Graphon at 25°C. was irreversibly adsorbed within a matter of minutes, even in absence of radiation. As shown by Figure 2, this monomer has a slow adsorption that is even more significant than that for furan. Throughout the 9 hours required for this experiment, there was always a detectable increase in the sample weight within a period of a few minutes. Probably this is analogous to the effect observed but not reported in detail by Smith, Pierce, and Cordes (8) in the adsorption of cyclohexene by Graphon.

In irradiation experiments with cyclohexadiene adsorbed on Graphon in an amount corresponding to 122% of a monolayer, the same erratic results were obtained that were obtained with furan adsorbed in excess of a monolayer. In all 4 irradiated cyclohexadiene samples, some of the monomer was fixed, but on the average half the cyclohexadiene could be removed in 24 hours.

Discussion:

The polymerization of monomers adsorbed on carbon black is of interest because the orienting effect of the solid surface on the monomer molecules can have a directing effect on polymerization. There are preliminary indications that this is actually observed in the case of furan (6). Special efforts are necessary to make studies of adsorption and subsequent polymerization as quantitative as possible. The thickness of the adsorbed layer, the orientation of the adsorbed molecules, and the temperature of the adsorbent are all variables that must be controlled. In previous work we had found that the adsorbed layer must be less than a monolayer for repeatable results to be obtained on radiation at 25°C. (6) and that the orientation of furan molecules is partially or completely "vertical" (plane of ring perpendicular to plane of

solid surface (5)). The present work indicates that an irreversible adsorption, believed to be a polymerization, occurs to the extent of 10 - 30% of the adsorbed furan per hour at 25° C. and half a monolayer. Lowering the temperature of the adsorbing surface did not prevent the irreversible adsorption. The phenomenon of irreversible adsorption is not limited to furan on carbon black; 1,4-cyclohexadiene also undergoes irreversible adsorption on carbon black.

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Table I

Possible Events to be Considered in Experiments
of the Ballentine-Manowitz Type

Free Monomer + Carbon black $\rightleftharpoons$ Monomer adsorbed on carbon black

Carbon black with defects $\xrightarrow{\text{radiation}}$ Carbon black with more defects

Adsorbed monomer + Carbon black with defects $\longrightarrow$ Chemisorbed monomer

Adsorbed monomer $\xrightarrow{\text{defects}}$ Adsorbed polymer

Adsorbed monomer $\xrightarrow{\text{radiation}}$ Adsorbed polymer

Adsorbed monomer $\xrightarrow{\text{defects}}$ Chain-initiating sites

Adsorbed monomer $\xrightarrow{\text{radiation}}$ Chain-initiating sites

Adsorbed monomer + chain-initiating sites $\xrightarrow{\text{post-polymerization}}$
Adsorbed polymer

Free monomer + chain-initiating sites $\xrightarrow{\text{post-polymerization}}$ Adsorbed polymer

Table II

Adsorption - Desorption Experiments without Radiation

Adsorbent: Graphon

Adsorbate: Furan

Temperature: 25-27°C.

Furan pressure: 22 torr

Fraction of a monolayer at equilibrium: 0.47

<u>Run No.</u>	1	2	3
Time allowed for adsorption, hr.	0.85	0.98	3.55
Amt. adsorbed, mg. /g.	15.0	14.9	29.2
Time allowed for desorption, hr.	1.00	4.25	6.05
Residual adsorbate at end of desorption, mg. /g.	1.5	5.2	20.1
Net desorption, mg. /g.	13.5	9.7	8.1

Table III

Effect of Postpolymerization in Radiation of Carbon Black
with Adsorbed Furan

Conditions: Furan equilibrated with Graphon to give 95% of a monolayer at 25-27°C. and irradiated with 100,000 rads of 6 m.e.v. electrons. Irradiation occurred within one hour of equilibration.

Time after irradiation when desorption was begun, hours	Fraction of a monolayer remaining on the Graphon after various periods of desorption			
	20 hours	40 hours	80 hours	200 hours
2	0.1	0.1	0.1	
26	0.7	0.6	0.4	0.3
49	0.90	0.90	0.85	0.80
73	0.95	0.95	0.95	0.90
96	0.95	0.95	0.95	0.90

Legend for Figures

Fig. 1: Adsorption isotherms, furan on Graphon, -18°C .

Fig. 2: Adsorption as a function of time, 1,4-cyclohexadiene on Graphon, 25°C .

References

- (1) D. S. Ballentine and B. Manowitz, U. S. Atomic Energy Commission, Brookhaven National Lab. Rept. No. 389(1956).
- (2) W. N. Reynolds, "Chemistry and Physics of Carbon", P. L. Walker, ed., vol. 2, p. 121, 1966.
- (3) A. Blumstein, Bull Soc. Chim. France 1961, 899.
- (4) V. V. Strelko and Z. Z. Vysotskii, Sintez i Fiz. Khim. Polimero 1964, 80.
- (5) H. K. Livingston and R. Senkus, J. Colloid Interface Science 30, 312 (1969).
- (6) H. K. Livingston and R. Senkus, J. Polym. Sci. Part B 7, 635 (1969).
- (7) C. Pierce, J. Mooi, and R. E. Harris, J. Phys. Chem. 62, 655 (1958).
- (8) R. N. Smith, C. Pierce, and H. Cordes, J. Am. Chem. Soc. 72, 5595 (1950).

MILLIGRAMS FURAN PER GRAM GRAPHON

MG. 1,4-CYCLOHEXADIENE PER GRAM GRAPHON