

Sorption of Poly(vinyl Acetate) on Cellulose. II. The Role of the Porous Structure

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Synopsis

The adsorption of poly(vinyl acetate) from benzene solution onto cellulosic materials having various porous structures was measured in an attempt to investigate the role of the pore size distribution in the sorption process. The variety of cellulose porous structures was obtained by combinations of different swelling agents—water, ethylenediamine, sodium hydroxide solution—with different subsequent drying treatments. The pore structure analysis was based on benzene desorption isotherms. The porosity of cellulose is responsible for selective adsorption of the smaller macromolecules from an unfractionated polymer solution. The amount of sorbed polymer increases when the polymer solution contains a greater fraction of lower molecular weight polymer. Only the pores above a certain size are accessible to the polymer. The amount of polymer sorbed is proportional to the area of such pores but is otherwise independent of the effects produced by swelling pretreatments.

INTRODUCTION

Few attempts have been made, either experimentally¹ or theoretically,² to investigate the role of pores in the sorption of macromolecules from solution onto a porous solid. In some cases³⁻⁸ it has been suggested that the porous nature of certain solids influences or determines the sorption kinetics, the fractionation of polymers due to selective adsorption, the variation of adsorption with molecular weight, and the different amounts of polymer sorbed on solids of similar area.

Adsorption is a surface phenomenon, and the significance of both external and internal surfaces of the solid is therefore obvious; but opinions differ as to the accessibility of "internal" surface to the macromolecules. Either the total surface has been considered accessible to the polymer,^{9,10} or the possibility of entering any kind of pores has been excluded, with only the external surface being involved.^{11,12}

While it is quite understandable that the surface existing in pores smaller than a limiting size is not accessible to certain macromolecules, the accessibility of the larger pores should be investigated, particularly when, as in swollen cellulose materials, the solid possesses a broad range of pores with dimensions from about 10 μ to several hundred angströms.¹³

The role of the porous structure in cellulose has been investigated in recent experiments¹³ dealing with the rate of dissolution of cellulose from a solid

cellulose substrate by a cellulase. A linear relationship was found between the initial rate of reaction and the surface area of the pores above 40 Å in diameter, thus indicating the limit in pore size accessible to this particular macromolecule.

The effect of variations in the pore structure of a cellulosic sorbent on the sorption of poly(vinyl acetate) from benzene solution has now been investigated in an attempt to determine the dependence of the amount of sorbed polymer on the volume and size of the pores and the accessibility of the pores to the macromolecules. Desorption isotherms of benzenes were employed to investigate the porous structure of the adsorbent as it existed in the benzene solution of the polymer.

EXPERIMENTAL

Materials

Sorbent. Standard laboratory blotters, consisting of a mixture of cotton and bleached sulfite hardwood and softwood fibers and having an α -cellulose content of 89.4%, an ash of 0.53%, and a Cu number 1.0 were used as strips $\frac{1}{4}$ in. wide. These were variously treated as described later.

Poly(vinyl Acetate). Three samples of poly(vinyl acetate) with average molecular weights (intrinsic viscosity) of 75,000, 50,000, and 5,000, respectively, were used in the study.

1. A commercial product (Gelva 15, Monsanto) prepared from vinyl acetate monomer. The number-average molecular weight, calculated by the manufacturer from osmotic pressure measurements, was given as 90,000. We also determined the average molecular weight from intrinsic viscosity measurements. The intrinsic viscosity $[\eta]$ in benzene at 30°C was found to be 0.590 dl/g, and the average molecular weight \bar{M}_η calculated from the equation $[\eta] = 56.3 \times 10^{-5} \times \bar{M}^{0.62}$ was 75,000.

2. PVAc 50, kindly supplied by Dr. Kuniak (Institute of Chemistry, Slovak Academy of Science, Bratislava). The intrinsic viscosity $[\eta]$ in benzene at 30°C was 0.470 dl/g, and the average molecular weight \bar{M}_η was 50,000.

3. A commercial product (Gelva 1.5, Monsanto) with an intrinsic viscosity $[\eta]$ in benzene at 30°C of 0.1115 dl/g and an average molecular weight \bar{M}_η of 5,000.

Solvents. Benzene was dried over sodium wire, distilled, and stored until use. Methanol was purified and dried by the ternary azeotropic distillation of its mixture with benzene and water. *n*-Pentane (Certified Reagent grade) was used without additional treatment.

Preparation of Sorbents

The porous structure of cellulose materials is quite sensitive to different kinds of treatment, and so a variety of sorbents could be obtained by treating samples of the same origin in the following ways.

TABLE I
Details of Sorbents and Polymers Used

Sample*	Swelling agent	State of sample prior polymer sorption	Polymer sorbed
1A	H ₂ O	saturated with benzene	
1B	EDA	saturated with benzene	Gelva 15
1C	NaOH, 18% w/w	saturated with benzene	
2A	H ₂ O	dried from benzene	
2B	EDA	dried from benzene	Gelva 15
2C	NaOH, 18% w/w	dried from benzene	
3A	H ₂ O	dried from water	
3B	EDA	dried from water	Gelva 15
3C	NaOH, 18% w/w	dried from water	
4	NaOH, 18% w/w	dried from <i>n</i> -pentane	Gelva 15
5	H ₂ O	saturated with benzene	Gelva 1.5
6	H ₂ O	saturated with benzene	PVAc 50

* Samples were swollen for 24 hr in water and ethylenediamine (EDA) and for 4 hr in NaOH solution.

The samples were swollen to different extents using either distilled water, anhydrous ethylenediamine, or aqueous 18% (w/w) sodium hydroxide solution. The swelling agents were removed from the samples by means of the solvent exchange method, using methanol as a replacement for water and ethylenediamine, and finally using benzene to replace methanol. The NaOH-swollen sample was washed in 1% acetic acid and water until neutral before the solvent exchange treatment. The solvent replacement was repeated at least five times over a period of several days.

The swollen and solvent-exchanged samples were divided into three parts and were used as follows in the polymer sorption experiments.

1. Directly, with no drying. These were the sorbents with the most open porous structure.

2. Dried from benzene under vacuum (10^{-2} torr) at 50°C. The porous structure of this sample was partially collapsed due to removal of benzene.

3. Dried as in (2) but then reswollen in water and dried from water at 105°C. These samples are almost nonporous because during water removal the previously developed porous structure collapsed completely.

In one case the water-swollen sample was solvent exchanged through methanol to *n*-pentane instead of benzene and dried from *n*-pentane under vacuum (10^{-2} torr) at 50°C in order to obtain a more open porous structure than by drying from benzene.

In Table I is a list of the sorbents with different pretreatments and the polymer samples sorbed on each.

METHODS

Sorption of Polymer

Two different methods were used. The first one, which was employed in all cases except for those involving samples 2A, 2B, 2C, and 4, has been

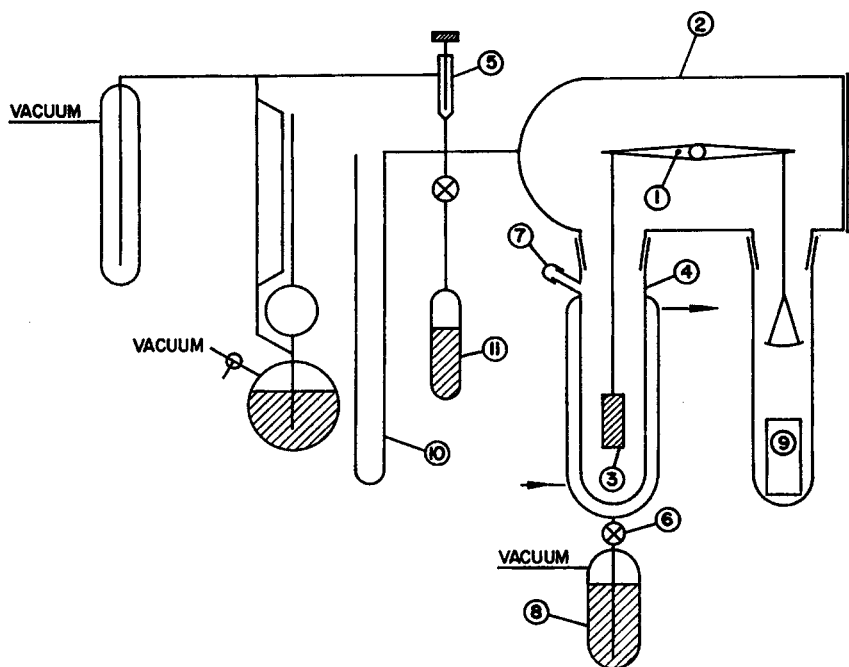


Fig. 1. Diagram of vacuum sorption apparatus for measuring both benzene sorption isotherms and polymer sorption. Components are identified in text.

described elsewhere.^{7,14} It was based on determination of the changes in polymer concentration in benzene solution before and after a sorption period. The second one, introduced by Patat et al.,¹⁵ is based on direct continuous weighing of the sample in the polymer solution. This method was found very suitable, particularly when the sample, after pretreatment and subsequent drying from benzene, must be immersed in the polymer solution out of contact with the air in order to avoid the possible influence of atmospheric moisture on the porous structure. The results of the two methods were found to be in acceptable agreement for comparable systems.

The weight changes of the sample as polymer was sorbed were obtained in the apparatus schematically shown in Figure 1. The weighing device was a Cahn RG Automatic Electrobalance (1) enclosed in a glass vacuum bottle (2). The sample (3) carrying an excess of benzene from the solvent exchange was transferred into the balance and was suspended from the balance beam into the temperature-controlled sorption tube (4). The benzene was then evaporated by applying vacuum through a Teflon needle valve (5), with final drying at 50°C for 48 hr. After drying the sample, the temperature was set as desired, the valve (5) was closed, and the sorption tube was filled under vacuum by benzene through a Teflon valve (6). When the sample was completely penetrated by benzene, as judged by its reaching constant weight, the vacuum was released. Using the opening

shown at 7, the stock solution of PVAc in benzene was added, and the change in weight was recorded over a period of 48 hr in order to determine when equilibrium had been reached and to determine the weight adsorbed.

A known amount of solution was removed to determine its concentration and density and an additional portion of the stock polymer solution was added to increase the concentration of PVAc for the next point on the sorption isotherm. The amount m of sorbed polymer was calculated from the formula

$$m = \frac{\Delta m d_{\text{pol}}}{d_{\text{pol}} - d_{\text{sol}}}$$

where Δm is the change in weight of the sample in polymer solution, d_{sol} is the density of solution, and d_{pol} is the density of sorbed polymer, which was found in previous work¹⁴ to be equivalent to the displacement density of polymer molecules in solution and to the density of solid PVAc (1.21 g/ml).

Sample 4 (Table I) was dried from *n*-pentane rather than from benzene, and only after final vacuum drying was the sample immersed in benzene as described above.

Benzene Desorption Isotherms

Benzene desorption isotherms were obtained for swollen samples that were duplicates of those used for polymer sorption. A special technique was used, based on the sorption apparatus schematically shown in Figure 1. The sample (3), after the swelling procedure and solvent exchange to benzene outside the apparatus, was transferred into the sorption tube (4) and suspended from the beam of the balance (1) inserted in the glass vacuum bottle (2). The sorption tube (4) contained about 150 ml benzene so that the sample was completely immersed. Then the vacuum was applied through a Teflon valve (5) to bring the pressure in the whole system close to the vapor pressure of benzene, and benzene from the sorption tube (4) was slowly transferred through the Teflon valve (6) into the reservoir (8) by means of vacuum.

When about 20 ml of benzene was left in the tube (4 in Fig. 1) the valve (6) was closed and the vacuum was applied through the valve shown at 5 in order to evaporate slowly almost all of the remaining benzene and also to remove all the remaining gases from the vacuum system. An open container (9) of P_2O_5 was kept in the system during the whole procedure in order to take up any free water vapor.

In this way the point was reached when the sample was in equilibrium with the saturated vapor of benzene, and this corresponded to the starting point of the desorption isotherm at a relative vapor pressure equal to unity. The vapor pressure was monitored by the mercury manometer (10). A stepwise lowering of the benzene vapor pressure was obtained by freezing out benzene vapor to the container shown at 11, and recording the change of weight of the sample provided the desorption isotherm. The equilibrium

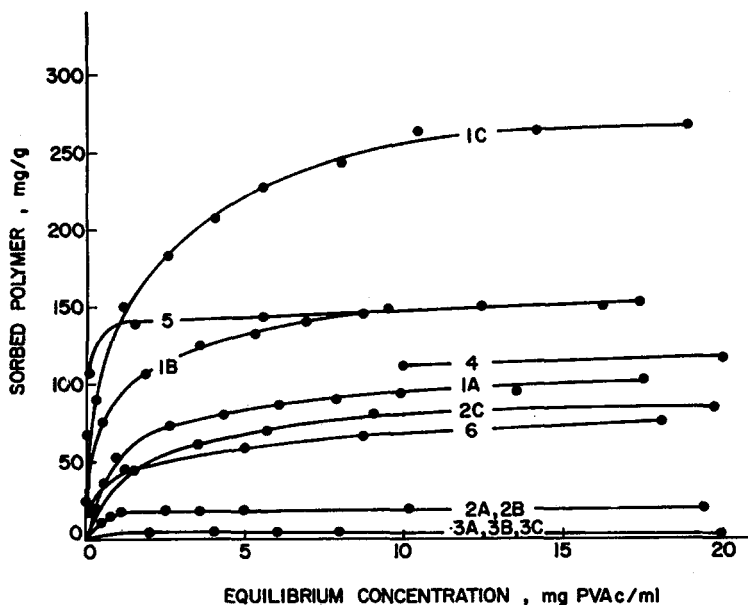


Fig. 2. Sorption isotherms for polymer from benzene solution onto pretreated cellulose samples. For identification of types of pretreatment and molecular weights of sorbates see Table I.

sorption of benzene for each point of the first desorption was achieved only after 48 hr. The dry weight of the sample was obtained after applying a vacuum of 10^{-2} torr and a temperature of 50°C .

When the first desorption was completed, the temperature of tube 4 was set again at 20°C , the benzene in container 11 was melted, the valve 5 was closed and the adsorption isotherm was measured by a stepwise increase of the benzene vapor pressure. The sample was then kept for at least 24 hr in saturated benzene vapor, and the second desorption isotherm was measured. The next step was to take the sample out of the balance, to immerse it in water for 24 hr and then to let it dry at room temperature with subsequent drying in an oven at 105°C for 2 hr. The oven-dried sample was immersed in benzene, transferred to the sorption apparatus, and again the desorption isotherm was measured.

Thus for each sample, three desorption isotherms were obtained: the first desorption from the swollen state, the second desorption after drying from benzene, and the third desorption after drying from water.

The *n*-pentane desorption-adsorption cycle was determined by the same method.

RESULTS

Polymer Sorption Isotherms

The sorption isotherms of the systems shown in Figure 2 are similar, with the amount of sorbed polymer increasing steeply at low concentrations and

TABLE II
Data for Benzene and *n*-Pentane

	Benzene (20°C)	<i>n</i> -Pentane (5°C)
Surface tension, dyn/cm	28.88	17.6
Density, g/cm ³	0.879	0.640
Mol weight	78.11	72.15
Temperature, °K	293	278
Gas constant	8.314 × 10 ⁷ erg/°C/mole	

approaching a plateau when the concentration is higher than 10 mg of PVAc per milliliter. The one exception is the isotherm obtained by using the polymer Gelva 1.5 (curve 5) which will be discussed later. The amount of sorbed polymer differs significantly according to the pretreatment to which samples of the same origin were exposed prior to the sorption of polymer. The highest level of sorbed polymer is regarded as a limiting value in each case and provides the basis for further discussion.

Porous Structure of Sorbents

The desorption isotherms of benzene were used to investigate and characterize the porous structure of the cellulose samples as they existed during sorption of polymer from benzene solution. The Kelvin equation was used for computation of the pore size distribution by assuming that the pores were cylindrical. An alternative assumption of infinite parallel-walled slits leads to an identical analysis, with the slit width replacing the pore radius. It was also assumed that the porous structure was rigid throughout the process of desorption. Although these conditions are not completely fulfilled, the method described is, in the light of present knowledge, the only one that can provide numerical data by a reasonably simple calculation. The measurements are reproducible, and the results provide a basis for comparing the porous structure of cellulose produced by various pretreatments of the same material.

The following relationships between the pore radius (or slit width) and the relative vapor pressure were used:

For benzene at 20°C:

$$r = \frac{-9.15}{\log P/P_0}$$

For *n*-pentane at 5°C:

$$r = \frac{-7.46}{\log P/P_0}$$

For computation of the pore radii from the Kelvin equation, the pertinent data for benzene and *n*-pentane are given in Table II.

The pore volume distributions were calculated from the desorption decrements at given relative pressures obtained from the isotherm. The correc-

TABLE III
Pore Analysis of NaOH-Swollen Sample

P/P_0^a	$r, \text{\AA}^b$	$\bar{r}, \text{\AA}^c$	$m,^d$ mg/g	$\Delta V^e X$ $10^3, \text{ml}$	$\Sigma \Delta V^f X$ $10^3, \text{ml}$	$\Delta A,^g$ m^2/g	$\Sigma \Delta A,^h$ m^2/g
Benzene							
0.95	416	—	668	—	—	—	—
0.90	199	307	638	34	34	2.2	2.2
0.85	129	164	606	36	70	4.4	6.6
0.80	94	112	575	35	105	6.3	12.9
0.75	73	84	538	42	147	10.1	23.0
0.70	59	66	500	43	190	13.1	36.1
0.65	49	54	458	48	238	18.0	54.1
0.60	41	45	415	49	287	21.7	75.8
0.50	30	36	333	93	380	51.8	127.6
0.40	23	26	280	60	440	46.3	173.9
<i>n</i> -Pentane							
0.95	339	—	464	—	—	—	—
0.90	162	250	438	41	41	3.2	3.2
0.85	105	134	416	34	75	5.1	8.3
0.80	79	92	398	28	103	6.1	14.4
0.75	60	70	380	28	131	8.1	25.5
0.70	48	54	356	38	169	14.9	37.4
0.65	40	44	332	37	206	17.0	54.4
0.60	34	37	308	38	244	20.3	74.7
0.50	25	30	256	81	325	55.9	130.6
0.60	19	22	198	91	416	82.4	213.0

^a Relative vapor pressure.

^b Pore radius from Kelvin equation at given relative pressure.

^c Average radius of pores within given relative pressure intervals.

^d Amount of sorbed benzene or *n*-pentane, read from the desorption isotherm at given relative pressure.

^e Volume increment desorbed.

^f Cumulative volume desorbed.

^g Surface area in pores of given average radius.

^h Cumulative surface area in all pores above the given radius.

tions, used in Pierce's method of pore size analysis,¹⁶ for the thickness of the multilayer film remaining on the pore walls at a given relative pressure, were omitted because of lack of data concerning benzene adsorption on cellulose.

From the volume ΔV of pores of known radius \bar{r} , the surface ΔA inside the pores was calculated using the relationship

$$\Delta A = \frac{2\Delta V}{\bar{r}}$$

Table III shows an example of the calculation, based on the first desorption isotherms obtained for the sample swollen in NaOH solution and subsequently transferred by solvent exchange to either benzene or *n*-pentane.

DISCUSSION

Studies of the adsorption of polymer from solution on to solids have led to the conclusion that the adsorption is basically controlled by the following factors: (1) interactions between polymer and solid, (2) interactions between polymer and solvent, and (3) interactions between solid and solvent.

However, in many cases, results do not correspond to expectations based on the interactions mentioned, and this is particularly apparent when the solid possesses a porous structure. The pores are probably responsible, to a great extent, for a selective adsorption of the macromolecules which are able to enter the pores, and thus the adsorbents may be regarded as a macromolecular sieve for fractionating polymers. The preferential sorption of lower molecular weight polymer fractions is in contrast to the frequently reported^{17,18} preferential adsorption of higher molecular weight polymer on nonporous substrates.

Molecular Weight of Polymer and the Sorption Isotherm

When comparing the adsorption of two unfractionated polymers, Gelva 15 (\bar{M}_η 75,000) and Gelva 1.5 (\bar{M}_η 5,000), and the fractionated PVAc 50 (\bar{M}_η 50,000) onto cellulose samples with the same pretreatment, i.e., the same porous structure, the differences in the shapes of the sorption isotherms and the extents of sorption are quite obvious (Fig. 2). In the case of Gelva 1.5 (curve 5), the limiting value of polymer sorption is reached at a lower equilibrium concentration, presumably because most of the macromolecules are small enough to enter the pores. Solutions of polymer Gelva 15 (curve 1A) do not contain enough of the smaller macromolecules at the lower concentration, and therefore the adsorption is completed only after the solution becomes sufficiently enriched with the fraction of lower molecular weight. The different amounts of sorbed polymer at the limiting value can be understood by recognizing that the solution of the Gelva 1.5 (curve 5) contains, in contrast to the Gelva 15, a proportion of such small macromolecules that they are able to enter pores inaccessible to any fraction of Gelva 15 macromolecules. As for the fractionated PVAc 50 (curve 6), the proportion of smaller macromolecules in comparison with Gelva 15 is decreased by fractionation, and therefore some of the pores available to the smaller of the Gelva 15 macromolecules are inaccessible to the PVAc 50, and consequently the limiting value of the sorbed polymer decreases.

This explanation, which means the selective adsorption of only that part of the macromolecules small enough to enter the pores of sufficient size, is supported by the measurement of the molecular weight of the sorbed polymer. In the case of Gelva 15, with \bar{M}_η 75,000, the average molecular weight \bar{M}_η of the sorbed polymer after extraction from the sample was found to be 20,000.¹⁹ Similar observations were reported¹ concerning the adsorption of polystyrene from carbon tetrachloride solution on nonporous Aerosil and various porous silica gels. The adsorption isotherms on Aerosil and on silica with comparatively large pores (750 Å) reached the limiting

value of sorbed polymer at low concentration, while the isotherm on silica with smaller pores (250 Å) showed slow increments of the sorbed polymer with increasing polymer solution concentration. From measurements of the viscosity of the supernatant solution, the preferential adsorption of the shorter macromolecules by narrow-pore silica was obvious, in contrast to a preferential adsorption of the longer macromolecules on the macroporous silica and nonporous Aerosil. In these latter cases, the polymer has free access to the surface.

Porous Structure and the Extent of Sorption

In order to investigate the role of pores of the solid in sorption process, the influence of the solvent-solute-solid interactions mentioned earlier was

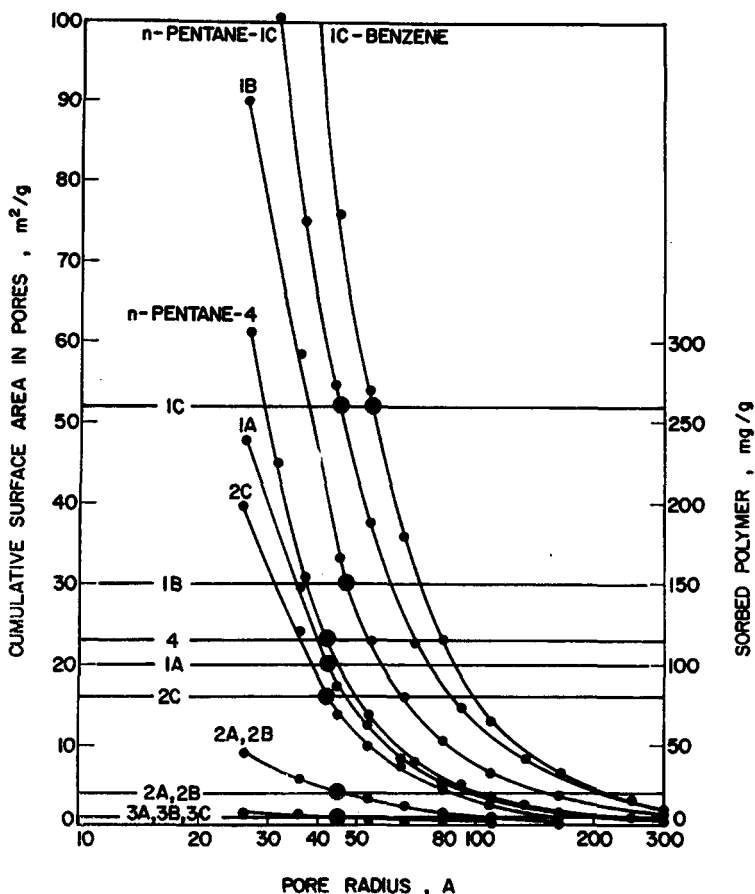


Fig. 3. Curves representing the cumulative surface area of the samples described in Table I and calculated from benzene or pentane desorption isotherms. Pentane was used only for samples 1C and 4. Horizontal lines represent the areas covered by sorbed polymer for the same samples. Intersections of lines and corresponding curves indicate radius of the smallest pores in which polymer sorption occurs.

TABLE IV
Comparison Amount of Sorbed Polymer with Surface Area in
Pores Above 45 Å in Radius

Sample ^a	Amount of sorbed polymer, ^b mg/g	Area covered by polymer, ^c m ²	Surface in pores above $r = 45 \text{ \AA}$, ^d m ² /g
1A	100	20	17.1
1B	150	30	33.1
1C	260	52	54.4
2A	20	4	4.1
2B	20	4	4.1
2C	80	16	13.8
3A	2-10	0.4-2.0	0.7-0.9
3B	2-10	0.4-2.0	0.7-0.9
3C	2-10	0.4-2.0	0.7-0.9
4	117	23	20.7

^a In cases 3A, 3B, and 3C, the extreme values from several measurements are given because of the experimental difficulties in obtaining more precise results.

^b From plateau in Figure 2.

^c As calculated assuming a specific sorption of 5 mg/m². See text.

^d From Figure 3.

reduced by using the same materials and sorption conditions. The only variability was in the porous structure of the sorbent obtained by various swelling pretreatments. The pore size distributions of those samples were calculated from benzene and/or *n*-pentane desorption isotherms, and the cumulative surface areas existing in pores as a function of the pore radii are plotted in Figure 3. The surface area is shown only for pores with radii above 26 Å because the analysis is not considered to be correct for the smaller pores.¹⁶

The next step was to calculate the area over which the adsorbed polymer is spread. In the previous work,¹⁴ we found that the decrease in internal surface, measured by water vapor sorption, was a linear function of the amount of polymer sorbed. This was interpreted as indicating a uniform layer of sorbed polymer. For standard blotters, this layer corresponded to a specific sorption of 5 mg/m². Based on the bulk density of the polymer, this corresponded to a layer of polymer of 42 Å. If the same specific sorption is used here to calculate the area covered by the polymer, the results shown in Table IV are obtained. If, further, these values are related to the corresponding areas in Figure 3, it is seen that in every case the coverage corresponds to the cumulative area of all the pores down to those about 45 Å radius. A comparison between the calculated coverage values and the cumulative surface of pores above 45 Å is shown in Table IV.

The results are thus consistent, and the conclusion may be drawn that all pores with radii above a certain value are accessible to the polymer. However, it must be emphasized that the nature of the assumptions is such that the numerical values that appear are not necessarily correct in the absolute sense. Indeed, it is immediately apparent that the uniform sorbed layer

thickness of 42 Å, previously deduced and used here, is inconsistent with sorption on the walls of pores of 45 Å radius or slits of 45 Å width. The reasons for the discrepancy, which reduces the significance of the results from quantitative to qualitative, may be found among the following:

1. The apparent specific coverage was calculated from the decrease in area accessible to water vapor and is subject to any uncertainties associated with this method.¹⁴

2. The assumption was made¹⁴ that the linear decrease in surface with polymer sorption was due to a sorbed polymer layer of more or less uniform thickness. An alternative explanation of the linearity is that the specific sorption may vary with the pore size but that the pore size distribution is similar in all samples. This possibility is suggested by the similarity of the curves in Figure 3. This alternative assumption does not alter the conclusions reached but allows for the possibility that the polymer sorption in the small pores may correspond to lower specific sorption values than for surfaces where sorption is not spatially restricted.

3. The analysis of the pore size distribution is based on the use of the Kelvin equation to calculate the pore dimensions and the volume and area of the pores. The dimensions were not corrected for the film thickness of the residual benzene after the capillary volume had been emptied.

4. The procedure for calculating pore size distributions is valid only if the porous structure is rigid and does not collapse during desorption. Some collapse almost certainly occurs during the first desorption of benzene from the completely swollen sample, since the second and subsequent desorptions occur at a lower level. This collapse during initial desorption cannot yet be taken into account. The slope of the isotherm on which the pore size calculation depends is greater or smaller, depending on whether the various pore sizes collapse simultaneously or consecutively. Since information on this point is not readily available, we have assumed that the pore size analysis is valid even for initial desorption isotherms.

The uncertainties concerning the assumptions, with the possible exception of the one concerning noncollapsibility, do not affect the qualitative interpretation of the results. The experimental methods have been applied to variants of the same material, and the comparisons are in good agreement. The results reported confirm the opinion that:

1. The preferential adsorption of the smaller macromolecules is due to the porous structure of the adsorbent.

2. The amount of polymer sorbed onto cellulose and the shape of the sorption isotherm are influenced by the porous structure of the adsorbent and the molecular weight distribution of the polymer.

3. There is a certain limit to the pore size below which polymer molecules are excluded but above which the pores of cellulose are accessible to a given polymer. The polymer sorbed is proportional to the area of the accessible pores but appears to be independent of any other effects produced by the swelling pretreatments.

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