

Porous Polymer Carbons. II. Preparation and Properties of Porous Poly(vinylidene Chloride) Carbons

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Synopsis

Suspension-polymerized copolymers of vinylidene chloride and ethylene glycol dimethacrylate have been converted into carbons by heating to 900°C. Poly(vinylidene chloride) homopolymer may melt on a first-stage heating at ca. 200°C and consequently yields a fused 900°C carbon; restraining the first-stage heating to slightly lower temperatures permits the retention of the polymer morphology which is then retained on subsequent carbonization at 900°C. The crosslinked copolymers do not fuse at 200°C and lose the dimethacrylate component, apparently cleanly, in the temperature range of 350–450°C and give 900°C carbons which are shrunken pseudomorphs of the parent polymer; all structural features are retained, including the characteristic skin of the polymer particles. Thus, the macroporous character of the carbons is controlled by both the crosslinker and diluent contents of the original polymerization recipe. The 900°C carbons are also microporous; hysteresis in nitrogen (77°K) isotherms is attributed to activated diffusion since carbon dioxide (196°K) isotherms are reversible. The microporosity of these dual-porosity carbons depends on the content of crosslinking comonomer in the parent polymer, and possible reasons for this dependence are discussed.

INTRODUCTION

In the preceding paper,¹ we described porous polymeric beads which were produced by the suspension copolymerization of vinylidene chloride and ethylene glycol dimethacrylate. We now report some studies of carbons produced from these precursor copolymers.

EXPERIMENTAL

Characterization techniques were as given in part I. Carbonizations were carried out in a Mullite tube placed in a vertical furnace (Stanton Redcroft VK2) fitted with a temperature program unit and a timer permitting predetermined isothermal heating periods. The samples were contained in carbon tubes located in the central, uniform-temperature region of the furnace and carbonizations were carried out in an atmosphere of oxygen-free nitrogen flowing at 100 ± 5 cm³/min. Quoted temperatures are the values from the furnace program unit and are considered to represent sample temperatures to $\pm 2^\circ$ up to ca. 350° and $\pm 5^\circ$ in the higher range. (Unless otherwise indicated, all degrees are °C.)

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Carbon nomenclature is by adding the final temperature of carbonization to the polymer designation; where chemical dehydrochlorination is used, an appropriate entry is also made. Thus, B/.250/.250/NH₃/350 is precursor polymer B/.250/.250 after dehydrochlorination by potassium amide in liquid ammonia followed by carbonization at 350°.

RESULTS

Several carbonization regimes were considered with the constraints that (i) a low temperature (150–200°) isothermal be included since it is in this temperature region that the first molecule of hydrogen chloride is eliminated in the decomposition of poly(vinylidene chloride),² and (ii) the final temperature be 800–900° to ensure complete removal of chlorine. A number of preliminary carbonizations were made and the products judged by their mercury intrusion curves. Semi-carbons (i.e., taken to 150°–200°) have macropore-size distributions similar to the parent polymer, whereas the distribution in full carbons shifts to large-pore sizes (Fig. 1). Variations in heating rates, holding times, and isothermal temperatures, within the ranges quoted above, produced only small changes in the pore distribution of the carbons. The conditions selected for "standard" carbonization were: heat to 200° at 60° hr⁻¹; hold at 200° for 18 hr; heat to 900° at 90° hr⁻¹; hold at 900° for 16 hr; natural cooling to room temperature. All these operations were conducted under flowing nitrogen.

Some samples were examined by differential scanning calorimetry (Perkin Elmer DSC 1) by heating at 32° min⁻¹ to 250°. Poly(vinylidene chloride) homopolymer exhibited a melting endotherm at 200°–203° in agreement with

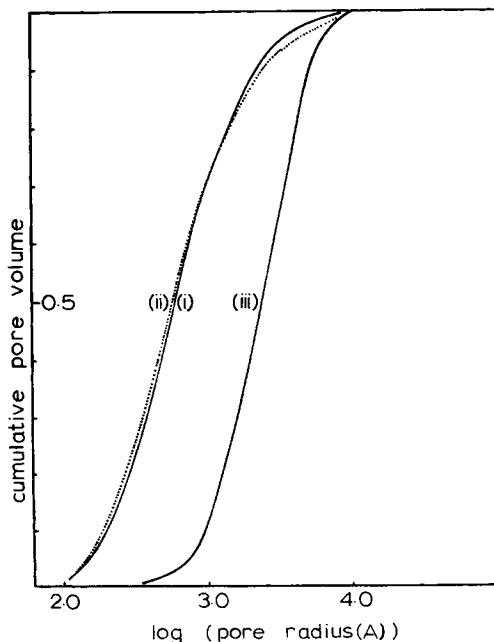


Fig. 1. Pore size distributions by mercury intrusion porosimetry: (i) original polymer (A/.333/.625); (ii) after 3 days, 150° air; (iii) as (ii) followed by heating in nitrogen at 40°/hr to 800°, 4 hr at temperature before cooling.

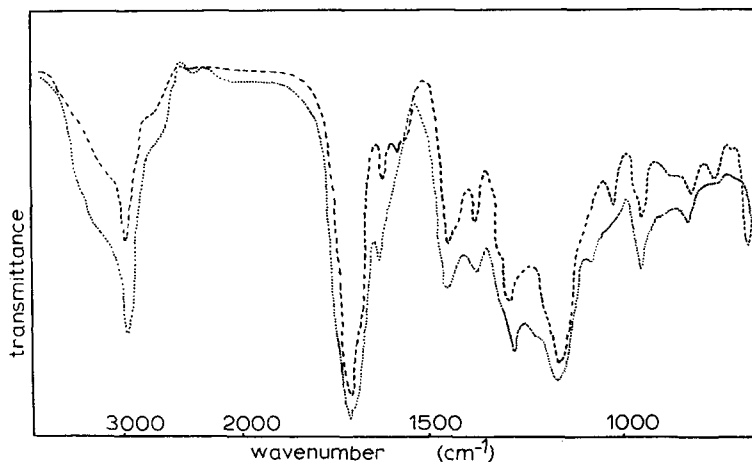


Fig. 2. Infrared spectra of pyrolysis product volatile 350–450°: (i) from vinylidene chloride-ethylene glycol dimethacrylate copolymer (-----); (ii) from polyethylene glycol dimethacrylate (.....).

the literature melting point,³ while copolymers had smaller endotherms in the same range of a size roughly proportional to their composition. Samples were examined visually after the DSC run; the homopolymer was perfectly black, whereas the copolymers varied from dark brown, at 0.125 volume fraction of crosslinker, to a fawn color at 0.500 volume fraction. These observations are consistent with an unzipping mechanism of dehydrochlorination⁴ in which the zip length is limited by the crosslinker units.

The carbon yields after heat treatment to 900°, relative to the vinylidene chloride content of the initial polymer, varied between 22.0% and 24.0%; the theoretical value for complete dehydrochlorination of poly(vinylidene chloride) is 24.5%. During the carbonization of copolymers, but not of the homopolymer (vinylidene chloride), a product distilled over between 350° and 450°. This distillate was an oil, pale yellow when formed at the lower end of the temperature range but darker when liberated at higher temperatures. For comparison, a polyethylene glycol dimethacrylate was prepared and taken through the carbonization procedure; again an oil was formed between 350° and 450°. The two products have very closely similar infrared spectra (Fig. 2) and behave almost identically on gas-chromatographic examination. The product formed during the pyrolysis of the vinylidene chloride-ethylene glycol dimethacrylate copolymers is thus identified as deriving from the latter component. The 900° carbon from the polyethylene glycol dimethacrylate was a flaky residue of less than 5% yield. Thus, during pyrolysis of the copolymer beads, the original crosslinking units are eliminated almost quantitatively without any significant associated loss of vinylidene chloride fragments.

Some copolymers were partially dehydrochlorinated by low-temperature (–33°) reaction with excess potassium amide in liquid ammonia by the method of Evans and Flood.⁵ Vigorous reaction started almost immediately after addition of the polymer beads, which rapidly turned brown-black; after about 3 hr, excess potassium amide was destroyed by addition of ammonium chloride, and the ammonia was allowed to evaporate. The ammonia semicarbons were washed

TABLE I
Elemental Analysis of Semi- and Full Carbons

Sample	C, %	H, %	Cl, %	N, %	O, % ^a
B/.000/.000/200	45.6	1.7	50.8	—	1.9
B/.250/.250/200	51.5	3.6	32.6	—	12.3
B/.250/.333/200	51.4	3.7	30.6	—	14.3
B/.250/.400/200	52.5	4.1	29.7	—	13.7
B/.250/.500/200	52.9	4.2	27.2	—	15.7
B/.250/.750/200	53.3	4.7	22.7	—	19.3
B/.160/.400/200	50.3	3.0	37.7	—	9.0
B/.250/.250/NH ₃ /350	81.6	4.1	3.1	1.7	9.5
B/.250/.400/NH ₃ /350	75.0	4.2	3.5	3.2	14.1
B/.250/.500/NH ₃ /350	n.d	n.d	n.d	4.5	n.d
B/.250/.750/NH ₃ /350	73.5	4.2	2.9	5.2	14.1
B/.000/.000/900	98.0	1.9	0.0	—	0.1
B/.250/.250/900	94.6	1.1	0.0	—	4.1
B/.250/.500/900	96.4	0.6	0.5	—	3.5

^a By difference.

thoroughly with water and subsequently with acetone before vacuum drying at 50°.

The elemental analysis of semi- and full carbons are given in Table I.

Heat treatment to a nominal 200° removes rather more than half the chlorine content of the original polymer. Chemical dehydrochlorination in liquid ammonia introduces some nitrogen into the structure, and some of this is still present after subsequent heat treatment to 350°, at which temperature nearly all the chlorine has been eliminated. The nitrogen is incorporated, probably as amide groups,⁶ to an extent dependent on the accessibility of the precursor polymer.

Carbonization to a 200° semicarbon does not remove the oxygen of the cross-linking comonomer units and slight traces of oxygen remain in the 900° copolymer carbons; however, the oxygen contents are estimated by difference only and so are particularly subject to error. The crosslinker oxygen is still largely present in the 350° semicarbons derived from chemically dehydrochlorinated copolymers.

The 200° products are the same size as the precursor, but shrinkage occurs at higher temperatures; the diameters of 900° carbon beads are approximately 35% less than those of the starting polymer. The 900° carbons may be removed from the furnace in a single piece but the beads separate on gentle rubbing between finger and thumb.

Homopolymer 900° carbons are normally obtained as a hard, fused rod; this behavior is identified with a first-stage heating at 200° or a little higher which melts the decomposing polymer. Homopolymer semicarbons consisting of separate unfused beads may be obtained by reducing the temperature of the initial isothermal to a few degrees below 200°. The tendency of poly(vinylidene chloride) to fuse on carbonization depends on the temperature at which the first stage of dehydrochlorination is carried out; this behavior has been described in the literature and has also been the subject of a separate study in these laboratories⁸ which will be reported later.

Apparent densities in mercury and in helium were determined; semicarbons were degassed at 200°, other carbons at 300°. As there is a possibility of some

TABLE II
 Pore Volumes^a of Polymer Carbons

Sample	ρ_{H_2} ^b	ρ_{He} ^b	Pore volume
B/.250/.250/200	1.05	—	—
B/.250/.333/200	0.76	—	—
B/.250/.400/200	0.69	—	—
B/.250/.250/NH ₃ /350	0.82	2.04 ^c	0.51
B/.250/.400/NH ₃ /350	0.62	2.04	0.90
B/.250/.500/NH ₃ /350	0.51	2.04	1.25
B/.250/.750/NH ₃ /350	0.59	2.04	0.98
B/.000/.000/900	1.19	2.03	0.35
B/.250/.000/900	1.22	2.04	0.33
B/.250/.250/900	0.91	2.03	0.60
B/.250/.333/900	0.69	2.09	0.97
B/.250/.400/900	0.61	2.06	1.15
B/.250/.500/900	0.53	2.05	1.39
B/.250/.750/900	0.63	2.03	1.09
B/.160/.400/900	0.82	2.04	0.73
B/.080/.400/900	1.05	2.03	0.46
B/.250/.250/G/900	0.98	2.04 ^c	0.53
B/.250/.333/G/900	0.78	2.04	0.83
B/.250/.400/G/900	0.66	2.04	1.02
B/.250/.500/G/900	0.61	2.04	1.14

^a In cm³/g.

^b In g/cm³.

^c Mean value assumed.

helium adsorption on certain carbons at room temperature,⁹ there is some uncertainty in the pore volumes calculated from the difference between the two densities. The experimental data are given in Table II.

The pattern by which the total pore volume of copolymer beads (Table I of ref. 1) varies with crosslinker content and with diluent content is carried over to the carbons; for example, see Figure 3. The fall in pore volume of sample B/.250/.750/900 may be attributed to its higher-than-expected mercury density; this sample has some very large pores ($r \geq 75000 \text{ \AA}$) so that some filling of the internal volume will occur at atmospheric pressure and so reduce the calculated pore volume. Semicarbons also exhibit the trend to higher pore volumes with increasing diluent content during the formation of the parent copolymer. The carbons, like the polymers, have pore volumes that increase with increasing crosslinker content in the original preparation.

The internal volume of pores of equivalent radii greater than 75 \AA may be estimated from mercury intrusion data, and the results are listed in Table III. The difference between these volumes and the corresponding values in Table II is the volume in small (less than 75 \AA equivalent radius) pores; as this is beyond the size region normally designated as micropores, we will describe this difference as a minipore volume.

It will be seen that B/.250/.750/900 has a lower apparent volume in large pores than the preceding sample; this is in line with the lower total pore volume data of Table II. Again, pore filling at atmospheric pressure could be the cause of the smaller volume. The 900° carbons derived from whole copolymer beads at a constant crosslinker content (volume fraction 0.250) have a constant mini-

TABLE III
Pore Volumes^a by Mercury Intrusion

Sample	Volume in pores \geq 75 Å radius	Minipore volume
B/.250/.250/NH ₃	0.20	—
B/.250/.400/NH ₃	0.47	—
B/.250/.500/NH ₃	1.01	—
B/.250/.750/NH ₃	0.95	—
B/.250/.250/NH ₃ /350	0.32	0.19
B/.250/.400/NH ₃ /350	0.76	0.14
B/.250/.500/NH ₃ /350	1.07	0.18
B/.250/.750/NH ₃ /350	0.82	0.17
B/.250/.000/900	0.05	0.28
B/.250/.250/900	0.32	0.28
B/.250/.333/900	0.70	0.27
B/.250/.400/900	0.87	0.28
B/.250/.500/900	1.10	0.29
B/.250/.750/900	0.81	0.28
B/.160/.400/900	0.40	0.33
B/.080/.400/900	0.11	0.35
B/.250/.250/G/900	0.37	0.16
B/.250/.333/G/900	0.69	0.14
B/.250/.500/G/900	0.93	0.21

^a In cm³/g.

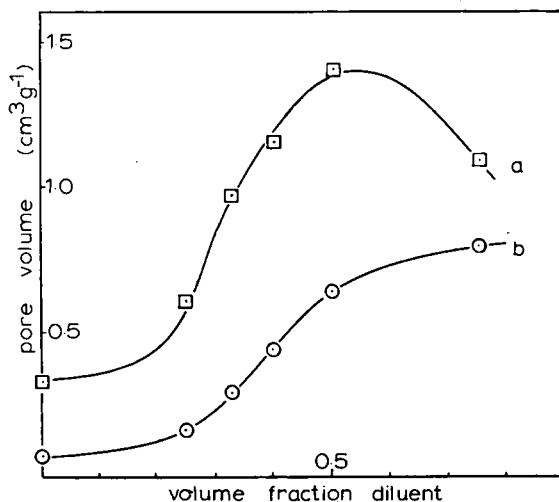


Fig. 3. Total pore volume (from difference between mercury and helium densities) as function of diluent content at polymerization, with constant (0.250) volume fraction of crosslinker (a) 900° carbons; (b) original polymers.

pore volume of 0.28 cm³/g, whatever the diluent content during polymerization. The minipore volume, however, seems to vary with crosslinker content and to tend toward the literature value¹⁰ of 0.40–0.42 cm³/g for the micropore volume of pure poly(vinylidene chlorides). That is to say, the crosslinking comonomer, which is eliminated from the structure by pyrolysis at 350–450°, partially restricts the development of smaller pores in the 900° carbon; the minipore

TABLE IV
Mean Pore Radii* by Mercury Intrusion

Sample	Radius
B/.250/.000/900	625
B/.250/.250/900	1520
B/.250/.333/900	5250
B/.250/.400/900	5600
B/.250/.500/900	12100
B/.250/.750/900	12000
B/.160/.400/900	9550
B/.250/.250/NH ₃ /350	575
B/.250/.400/NH ₃ /350	2000
B/.250/.500/NH ₃ /350	10500
B/.250/.750/NH ₃ /350	10000
B/.250/.250/G/900	1900
B/.250/.333/G/900	3900
B/.250/.500/G/900	12600

* In Å.

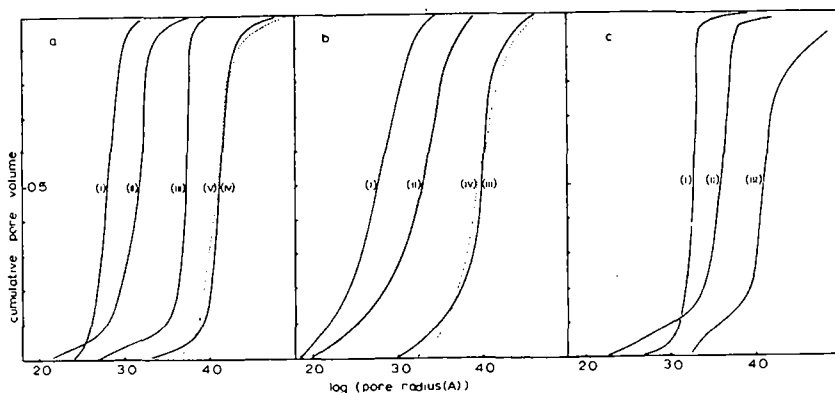


Fig. 4. Pore size distributions by mercury intrusion porosimetry: (a) 900° carbons from whole beads, (i) B/.250/.000/900, (ii) B/.250/.250/900, (iii) B/.250/.333/900, (iv) B/.250/.500/900, (v) B/.250/.750/900; (b) 350° semicarbons, (i) B/.250/.250/NH₃/350, (ii) B/.250/.400/NH₃/350, (iii) B/.250/.500/NH₃/350, (iv) B/.250/.750/NH₃/350; (c) 900° carbons from fractured beads, (i) B/.250/.250/G/900, (ii) B/.250/.333/G/900, (iii) B/.250/.500/G/900.

volumes found for 350° semicarbons suggest that rather more than half this volume has been created in the lower-temperature region.

Some pore-size distributions from mercury intrusion are shown in Figures 4a-4c. The macroporous structure of the carbons is clearly determined by the formulation of the original polymerization; however, both 350° and 900° carbons from polymers made at diluent volume fraction 0.750 have distributions closely similar to those from 0.500 diluent content polymers. The 900° carbon beads are so hard that it was impossible to fracture them just sufficiently to open up the interior structure without completely destroying structural coherence. Representative precursor beads were lightly ground and then carbonized; the similarity of the pore size distributions of Figures 4a and 4c suggests that the anomalies found with polymer beads are not evident with the resulting carbons. Mean pore radii (i.e., at 50% pore filling by mercury intrusion up to a maximum pressure of 1000 atm) are presented in Table IV.

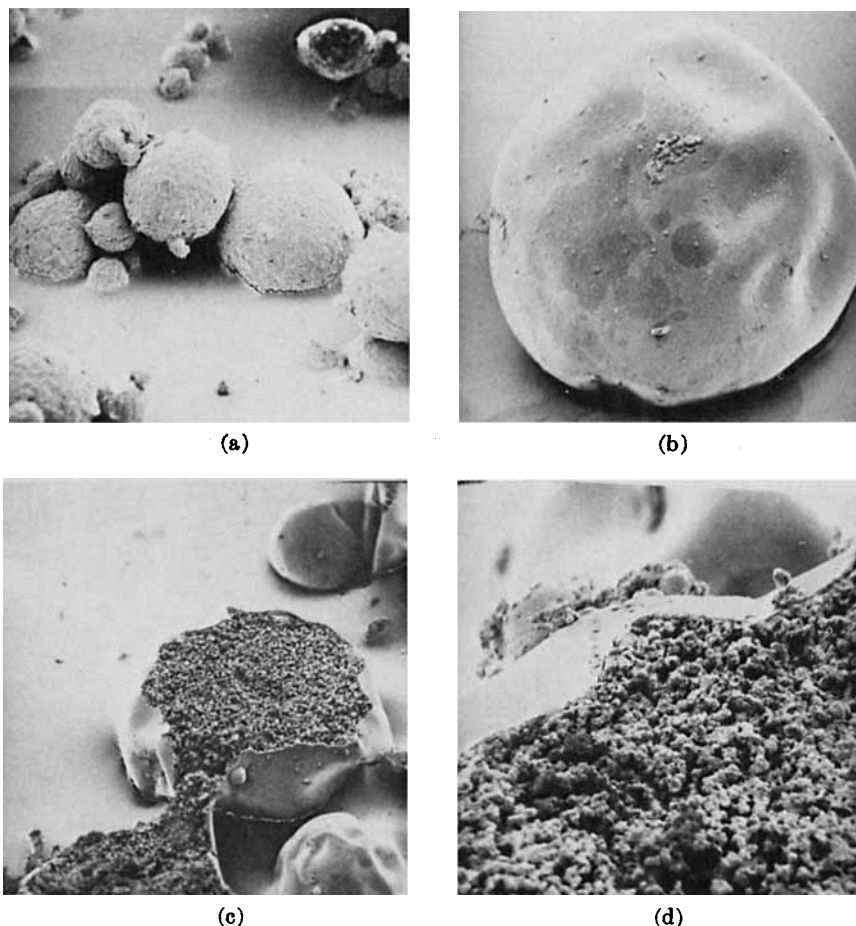


Fig. 5. Scanning electron microscopy of semi-carbons. (a) B/.000/.000/200 ($\times 310$); (b) B/.250/.400/.200 ($\times 350$); (c) B/.250/.400/.200 - bead cut open ($\times 140$); (d) B/.250/.400/.200 ($\times 1430$).

As with the precursor polymers, scanning electron microscopy is of great value in structural studies. First, the semicarbons obtained by heat treatment to an 18-hr isothermal at 200° (nominal) are considered. Figure 5a shows beads of poly(vinylidene chloride) homopolymer after such partial carbonization at a little below the polymer melting temperature of ca. 200° ; the beads have retained the open external surface found in the precursor polymer (cf. Fig. 6a of ref. 1). A semicarbon from a crosslinked polymer (B/.250/.400/.200, Fig. 5b) has the structureless outer surface of the parent polymer (cf. Figs. 5a and 6b of ref. 1). When semicarbons are split open with a razor blade, the porous interior structure becomes visible as in Figure 5c; the skin formed on crosslinked polymer beads (cf. Fig. 7d of ref. 1) persists in 200° carbons as seen in Figure 5d. Within the thin skin is a uniform arrangement of agglomerated microglobules.

The structural features of the original preparations are also preserved in semicarbons obtained by low-temperature chemical dehydrochlorination and in these products after heating at 350° .

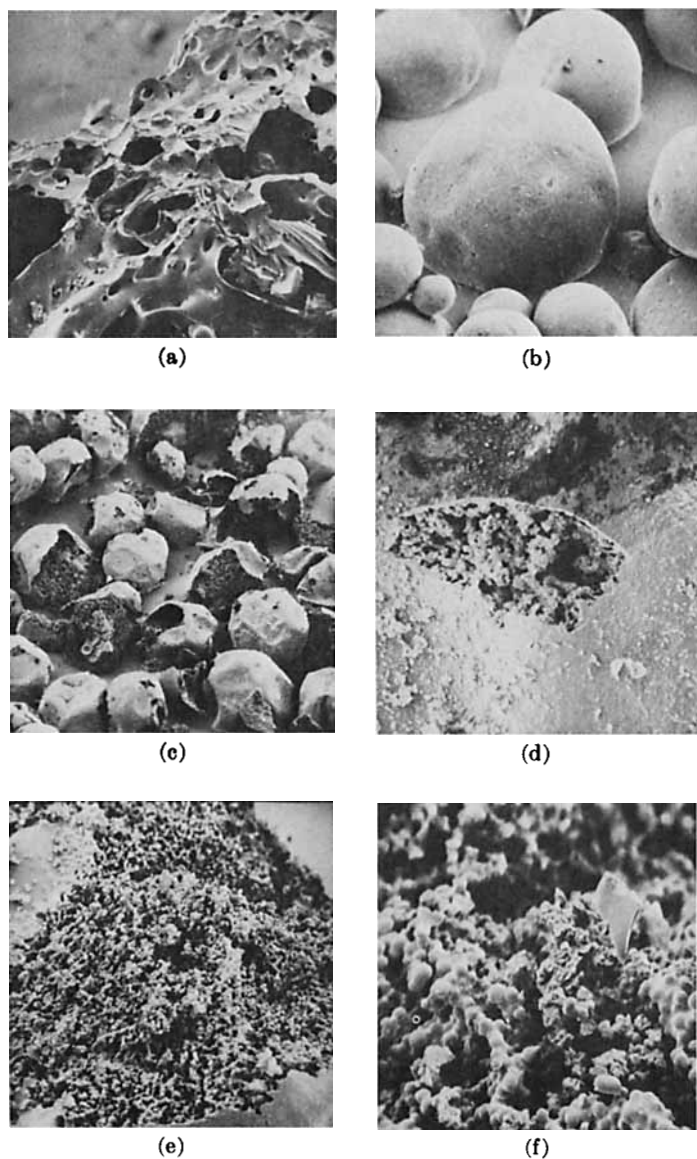


Fig. 6. Scanning electron microscopy of 900° carbons: (a) B/.000/.000/900 ($\times 120$); (b) B/.250/.250/900 ($\times 100$); (c) B/.250/.500/900—scraped with razor blade ($\times 43$); (d) B/.250/.333/900 ($\times 1040$); (e) B/.250/.500/900 ($\times 215$); (f) B/.250/.500/900 ($\times 860$).

Carbonization of homopoly(vinylidene chloride) at 900° after preliminary heating around the polymer melting point yields a fused rod of carbon with open appearance (Fig. 6a). It is not clear whether the foamed structure is produced by the expulsion of the hydrogen chloride (blow holes) or by the flow of the softening beads; the pieces of carbon exhibit some birefringence on examination between crossed polars in a low-power microscope. On the other hand, cross-linked beads, although shrunken, retain their shape and internal structure on heating to 900° (Fig. 6b). The preceding paper described how polymer beads

TABLE V
Mean Radii^a of Interior Microglobules

Sample	Radius
B/.250/.400/200	3500
B/.250/.250/900	<1500
B/.250/.333/900	1500
B/.250/.400/900	2000

^a In Å.

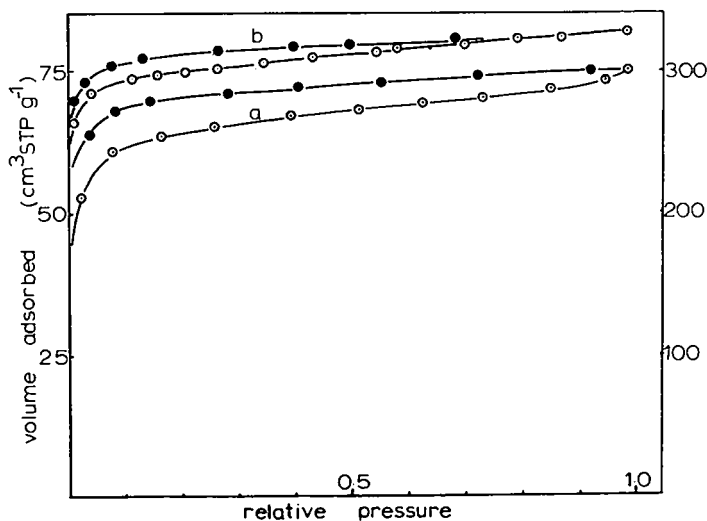


Fig. 7. Adsorption isotherms, N₂, 77°K: (a) B/.250/.400/900 (left-hand scale); (b) BCRA PVDC carbon (right-hand scale); filled symbols, desorption.

formed at high diluent contents had a deformed spherical appearance (cf. Fig. 5b of ref. 1); these features carry through to the 900° carbons (Fig. 6c). The carbon beads of Figure 6c had been scraped with a cutting edge to expose the interior structure. In 900° beads, the surface skin is thin (Fig. 6d); a small fracture in this sample enables the open internal structure to be seen. These internal features of 900° carbons derived from crosslinked beads are very similar to the parent structure (cf. Figs. 7c and 7d of ref. 1) and are an agglomeration of rounded microglobules (Figs. 6e and 6f). It was possible to make only approximate estimates of microglobule size since the resolution of the scanning electron microscope was less good at higher magnifications. However, the constituent microglobule dimensions are noticeably smaller than those of their parent polymers (Table V).

Attempts to examine the carbons by transmission electron microscopy failed because suitable sections could not be cut. Neither glass nor diamond microtome knives would section the hard, open carbons, and micrographs seemed to show only the stacked fragments of shattered microglobules.

Nitrogen (77°K) adsorption isotherms of 900° carbons from crosslinked precursors were somewhat irreproducible and showed extensive low-pressure hysteresis (Fig. 7a). The fused carbons from poly(vinylidene chloride) homopolymer, however, gave isotherms of acceptable reproducibility with only slight hysteresis

TABLE VI
Nitrogen Isotherm Data of 900° Carbons

Sample	BET area, m ² g)	Micropore volume, cm ³ /g
PVDC carbon*	1145	0.468
PVDC carbon*	1203	—
B/.000/.000/900	956	0.393
B/.250/.250/900	227	0.100

* BCRA sample of stated area 1200 m²/g.

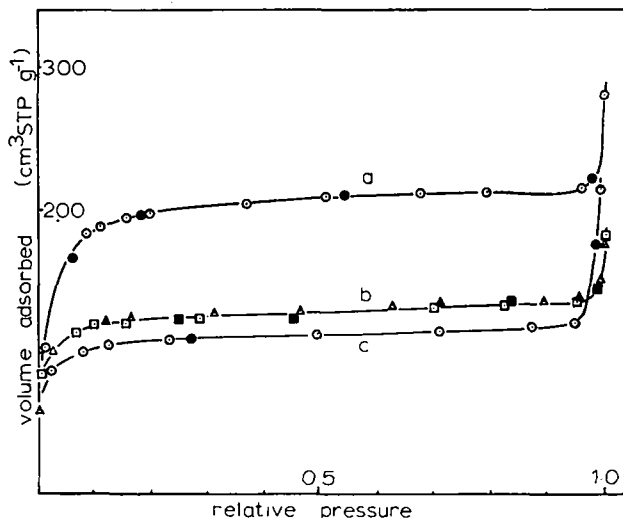


Fig. 8. Adsorption isotherms, CO₂, 195°K: (a) B/.000/.000/900; (b) B/.250/.250/900 (two determinations); (c) B/.250/.750/900; filled symbols, desorption.

(Fig. 7b). The isotherms are typical of microporous solids: although apparent surface areas may be obtained by application of the BET equation, it was noticed that the monolayer capacity so obtained fell well below the visually judged "point B" of the isotherm. Therefore, micropore volumes were also determined by fitting the data to the Langmuir equation, and these are recorded in Table VI.

The difficulties experienced with carbons from crosslinked polymers were attributed to activated diffusion effects so that, following the recommendations of Marsh and Wynne-Jones,¹¹ further isotherm measurements were made with carbon dioxide at 195°K as adsorbate. The 900° carbons have reversible CO₂ isotherms (Fig. 8) without detectable hysteresis, and so may be presumed to contain little internal volume in pores of equivalent radii greater than ca. 15–20 Å and less than ca. 400 Å. Micropore volumes were estimated from the Langmuir plots of $(p/p_0) \cdot V^{-1}$ against p/p_0 , which were extremely linear. These volumes are close to the so-called point B of the isotherm and to the micropore volume found from the equation

$$\log V = \log V_m - D (\log p_0/p)^2$$

of Dubinin.¹² The micropore volumes so calculated from the CO₂ adsorption isotherms are given in Table VII.

TABLE VII
Micropore Volumes from CO₂ Isotherms

Sample	Micropore volume, cm ³ /g
PVDC carbon (BCRA)	0.462
B/.000/.000/900	0.352
B/.250/.000/900	0.233
B/.250/.250/900	0.209
B/.250/.333/900	0.266 (0.140) ^a
B/.250/.400/900	0.193 (0.178)
B/.250/.500/900	0.196
B/.250/.750/900	0.184 (0.160)
A/.125/.000/900	0.296
A/.200/.375/900	0.253
A/.250/.500/900	0.228
A/.333/.625/900	0.210
A/.500/.750/900	0.185
A/.625/.800/900	0.175

^a Values in parentheses refer to samples measured after three months of storage.

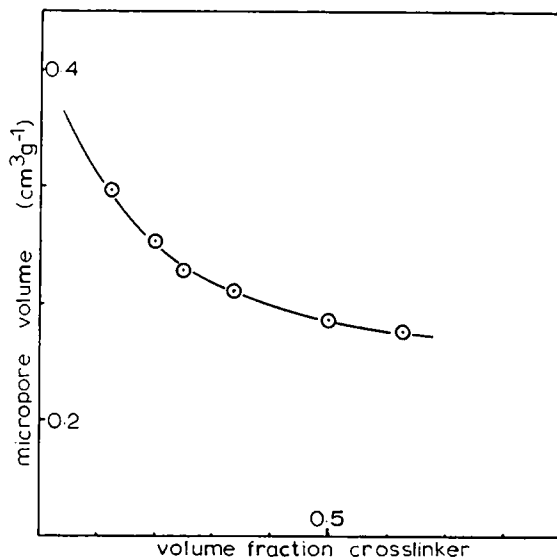


Fig. 9. Micropore volume of 900° carbons as function of ethylene glycol dimethacrylate content in precursor copolymer.

Carbons which have copolymer precursors of crosslinker volume fraction 0.250 show rather similar adsorbed volumes of CO₂ with little influence from the diluent content at the polymerization stage. As explained earlier,¹ there may be a slight increase in effective crosslink density through the B/.250/- series of copolymers, and the microporosity shows a similar trend. Thus, the macroporosity of the carbons is controlled by both the crosslinker and diluent content at polymerization, but the microporosity depends on the former factor, that is, the chemical composition of the copolymer. Figure 9 illustrates the dependence of the micropore volume from CO₂ adsorption on the crosslink content in the precursor polymer. This micropore volume tends to be a little less than the "mini-pore" values quoted in Table III. Aged carbons had reduced CO₂ adsorptions;

although stored in vacuum desiccators, it may be that some chemisorption of oxygen had taken place. For the same reason, the nominally "fresh" samples may yield lower than their true micropore volumes.

The macroporous structure of 900° carbons is evident in the rate of CO₂ adsorption; with the least macroporous samples, the equilibration time could be twice as long as with the more open carbons.

The 350° carbons from polymers which had been partially dehydrochlorinated by potassium amide in liquid ammonia also have type-I CO₂ isotherms but with microporosities about half that of the 900° carbons. The 200° semicarbons adsorb CO₂ at 195°K very slowly, which suggests the presence of some pores of small radius. Reliable estimates of surface areas could not be obtained, but the approximate values lie in the range of 10–25 m²/g depending on the sample macroporosity; these areas, although small, are larger than those of the parent polymers.

DISCUSSION

The carbonization profile incorporates an 18-hr isothermal at ca. 200°; in this first stage of pyrolysis, rather more than half the total dehydrochlorination takes place. During the second heating process, to 900°, the ethylene glycol dimethacrylate crosslinking moieties are decomposed between 350° and 450° and volatilize, apparently completely, as compounds which are tars at room temperature. No significant loss of carbon associated with the vinylidene chloride residues is found. Under the carbonization conditions used in the present work, vinylidene chloride homopolymer fuses unless the first-stage heating is made below the polymer melting range. Whether or not such fusion occurs during carbonization depends on the nature of the initial heat treatment.^{7,8} If taken rapidly to temperatures in the region of the homopolymer melting point, fusion starts during the initial dehydrochlorination. If held at lower temperatures until the first molecule of hydrogen chloride (per repeat unit) has been eliminated, subsequent heating does not give a fused carbon. A poly(vinylidene chloride) chemically dehydrochlorinated at -33° did not fuse on subsequent heating to 450°.

Copolymers of vinylidene chloride and ethylene glycol dimethacrylate prepared by suspension polymerization¹ give products of characteristic morphology. The morphological features are retained, albeit in a shrunken form, in the derived carbons; both crosslinked polymers and their carbons have a microglobular structure enclosed in a surface skin. The macroporous nature of the carbons is related to that of the parent polymers and is determined by the amount of crosslinking comonomer and diluent present at polymerization; the average macropore dimensions, total porosity, accessibility, and (presumably) mechanical strength of the carbons are readily controlled by suitable adjustment of the polymerization recipe.

The desorption hysteresis shown by carbons to N₂ at 77°K persists into the low-pressure region. The extent of this hysteresis is greater with copolymer carbons than with homopolymer carbons. Everett and co-workers⁷ have suggested that it is the intercrystalline gaps in homopoly(vinylidene chloride), presumed to be a few hundred Å across, which persist during nonfusing carbonization to form the pores responsible for sorption hysteresis. The present data do

not permit a direct examination of this suggestion since unfused carbons are normally derived only from copolymers. However, all carbons which show hysteresis to nitrogen at 77°K have reversible isotherms with carbon dioxide at 195°K; we attribute the nitrogen hysteresis solely to activated diffusion effects. Further, the copolymer carbons have a dual porosity; the macropores are too large, and the micropores too small, to show the desorption hysteresis attributed to the emptying of liquid-filled capillaries.

The magnitude of the micropore volume of 900° carbons depends on the composition of parent copolymer (Fig. 9), even though the comonomer which restricts the formation of the micropores is eliminated at intermediate temperatures. Carbons from highly crosslinked copolymers still have considerable micropore volume accessible to CO₂ at 195°K. The processes by which the micropores are formed are not clear; however, some salient points may be recorded. Micropores barely start to form at 200° and so are not associated with the first dehydrochlorination process. Roughly half the micropores have been formed at 350°, at which temperature the dimethacrylate crosslinking units are still present. The evidence on 350° carbons is based solely on samples previously dehydrochlorinated chemically, and we assume that thermally (200°) treated copolymers would behave similarly. The rest of the micropores are formed at higher temperatures where the crosslinking residues have been lost.

Two principal factors might be associated with the role of the ethylene glycol dimethacrylate in affecting the micropore volume in fully carbonized samples. First, the increase in crosslinking comonomer is at the expense of polymer crystallinity; this implies that micropores are derived from the well-ordered structural regions of the precursor polymer. Secondly, there is the effect of crosslinking units on the mobility of chain segments and their ability to undergo reorganization. This is not simply that the dimethacrylate units hold the chains in place below 350–450°; the second dehydrochlorination step also forms interchain links below this temperature region. An interesting observation may be interpolated here; if vinylidene chloride is replaced by acrylonitrile in the copolymer formulation and the product pyrolyzed, the carbon yield at 450° is zero. The dimethacrylate units are removed as before but the acrylonitrile interchain linking is insufficient to prevent the volatilization of the relatively short-chain segments, which are derived from acrylonitrile units, lying between the dimethacrylate junctions.

It may be assumed that the presence of "chemical" crosslinks below ca. 350° will influence the number and arrangement of the "degradation" crosslinks formed up to this temperature and, in turn, the chain mobility throughout the whole temperature span of carbonization. That is, the ethylene glycol dimethacrylate units of the parent polymer have the effect of restricting chain mobility during the entire carbonization process and that this limits micropore development. Under the pyrolysis conditions employed, vinylidene chloride homopolymer, initially highly crystalline, goes through a stage of high chain mobility such that a fused carbon results; this carbon is highly microporous.

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References

1. G. J. Howard and S. Knutton, *J. Appl. Polym. Sci.*, **19**, 683 (1975).
2. D. H. Everett, E. Redman, A. J. Miles, and D. H. Davies, *Fuel*, **42**, 219 (1963).
3. R. D. Bohme and R. A. Wessling, *J. Appl. Polym. Sci.*, **16**, 1761 (1972).
4. S. S. Barton, G. Boulton, B. H. Harrison, and W. Kemp, *Trans. Faraday Soc.*, **67**, 3534 (1971).
5. B. Evans and E. A. Flood, *Can. J. Chem.*, **45**, 1713 (1967).
6. J. J. Bohrer, *Trans. N. Y. Acad. Sci. Ser II*, **20**, 367 (1958).
7. L. B. Adams, E. A. Boucher, R. N. Cooper, and D. H. Everett, 3rd Conf. Ind. Carbon & Graphite, London, 1970, p. 478.
8. S. Szynaka, M. S. Thesis, University of Manchester, 1972.
9. J. J. Kipling, J. N. Sherwood, P. V. Shooter, N. R. Thompson, and R. N. Young, *Carbon*, **4**, 5 (1966).
10. E. Greenhalgh, B. J. Miles, E. Redman, and S. A. Sharman, 2nd Conf. Ind. Carbon & Graphite, London, 1965, p. 405.
11. H. Marsh and W. F. K. Wynne-Jones, *Carbon*, **1**, 269 (1964).
12. M. M. Dubinin, *Chem. Rev.*, **60**, 235 (1960).

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