Isotropic carbon spherulite formation by pressure carbonization of divinylbenzene

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Abstract. Carbonization of divinylbenzene (DVB) polymers was carried out in sealed gold or palladium–silver alloy capsules in a hydrothermal apparatus under pressures up to 2·07 kbar and temperatures up to 900°C. The polymers used were prepared at atmospheric pressure with catalyst or under pressures up to 8·27 kbar. Pressure polymerization proceeded rapidly without catalysts and yielded hard non-porous dense pieces. The carbons prepared by carbonization of polymers up to 900°C were further heated up to 2200°C in flowing helium at atmospheric pressure. Samples were characterized by x-ray and electron diffraction; infrared, optical, and scanning electron microscopy; and measurements of densities and refractive indices. It was found that the morphology of the carbons was strongly affected by the pressures of polymerization and carbonization, the permeability of the capsule material to hydrogen during carbonization, and the addition of vinylferrocene. Carbons obtained under a certain range of pressure and temperature consisted of isotropic spherulitic particles up to 10 μm in diameter. Carbons produced by treating the same polymer at atmospheric pressure in flowing nitrogen were also isotropic, but gave no indication of spherulitic bodies. In the same temperature range, but at pressures above about 1·5 kbar, a new carbon morphology, approaching the periodic minimal surface form of interconnecting solids, was obtained. In this new form the carbon displayed preferred orientation to a small degree, as seen by electron diffraction, and was no longer optically isotropic.

1 Introduction

Pyrolysis of organic compounds, the first step in the production of cokes or chars, is generally conducted under reduced or atmospheric pressures. The use of low pressure seems to be logical for producing high carbon residues by favoring the formation and escape of volatiles. However, decomposition, as manifested in the volatiles, is only one feature of pyrolysis and not necessarily the most important. Others are molecular rearrangement and increase in molecular weight, and with these the effect of pressure cannot be easily predicted. Any conditions which would favor molecular rearrangement or increased molecular weight may also favor a high degree of carbon–carbon crosslinking or carbon-packing density. Pressure does control solubility, viscosity, density, and phase separations within the system during polymerization and carbonization, all of which may influence the kind and degree of crosslinking in the polymer and carry through pyrolysis and carbonization.

Carbonization of well known organic compounds under moderate pressures has been reported by several investigators. Walker and Weinstein (1967) found that samples prepared from the carbonization of anthracene, phenanthrene, and their mixtures by first coking in a stainless steel autoclave to 550°C, followed by coking in a nitrogen flow at 900°C, were all highly graphitizable when taken to 2500°C. Weintraub and Walker (1971) also studied the carbonization of mixed organic compounds, anthracene–biphenyl and phenanthrene–biphenyl, in a similar autoclave system, with the aim of controlling the degree of graphitizability of the carbons formed. The addition of biphenyl to the phenanthrene was found to produce a greater decrease in graphitizability than comparable additions of biphenyl to anthracene. The results were explained

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primarily on the basis of similar carbonization rates for phenanthrene and biphenyl, and markedly different carbonization rates for anthracene and biphenyl.

Marsh, *et al.*, (1971) reported the carbonization of anthracene under pressures up to 2·6 kbar. They found the formation of a spherulitic carbon, about micrometer-sized, which is essentially the anisotropic mesophase described originally by Brooks and Taylor (1965, 1968). It was found that pressure carbonization enhanced moderately the subsequent graphitizability of the carbon. A study of the effect of pressure during carbonization of resins on their subsequent graphitizability was also reported by Kotosonov, *et al.*, (1969). They applied a uniaxial mechanical pressure (0–500 kg cm^{-2}) on a phenolfurfuryl-formaldehyde resin and found that in the temperature range 400 to 600°C the use of pressure markedly influenced the graphitizability of the carbon formed. Bradshaw, *et al.*, (1967) recognized the effect of pressures between 0·14 and 0·69 kbar on the characteristics of the products formed during the curing and pyrolysis of an aromatic precursor resin derived from naphthalenodiol.

It appears that carbonization at high pressures may influence the crystallite orientation and thereby afford the possibility of producing carbons of different morphologies. In the present work, pressure polymerization and carbonization, followed by heat treatment up to 2200°C, of divinylbenzene (DVB) with or without small additions of vinylferrocene were conducted. The effects of pressure and permeability of the capsule material to hydrogen within a hydrothermal apparatus were of particular interest.

2 Experimental
The DVB used was obtained from K and K Laboratories, Inc. (Plainview, New York) and vacuum distilled before use. The vinylferrocene to be formulated with DVB was obtained from Research Organic–Inorganic Chemical Co. (Sun Valley, California).

All pressure work, except experiments at 8·27 kbar, was carried out in a hydrothermal apparatus of the cold seal type. A hydraulic compressor actuated by compressed air was used to generate water pressures up to 4·3 kbar in a Stellite 25 reactor. Experiments at the pressure of 8·27 kbar were performed using a high-gas-pressure apparatus similar to that described by Yoder (1950). Samples were hermetically sealed into thin-walled noble-metal tubes, 2·5 mm or 5 mm in diameter. Gold tubing is impermeable to hydrogen, whereas palladium–silver alloy tubing is permeable under the conditions of the experiments. These two materials were chosen to afford another means of possibly influencing the progress of polymerization and pyrolysis.

Experiments consisted of two processes—polymerization and carbonization. First, DVB was polymerized in air at atmospheric pressure with azobisisobutyronitrile as a catalyst, or under hydrostatic pressures up to 8·27 kbar at temperatures up to 300°C without catalysts. A standard heating rate of 3·5 K min^{-1} was followed. Some polymerizations included 2 to 10 wt.% vinylferrocene in order to study its influence on the properties of carbon formed. Carbonization of polymers and copolymers so formed was carried out at various temperatures up to 900°C in flow of atmospheric-pressure nitrogen or in sealed capsules under hydrothermal pressures up to 2·07 kbar. A heating rate of 6·5 K min^{-1} was used in all these preparations. Samples prepared up to 900°C were further heat treated in a flow of atmospheric-pressure helium up to 2200°C for 3 h, using a heating rate of 1·5 K min^{-1} to reach maximum temperature. Samples produced were characterized using the techniques described below.

2.1 *Scanning electron micrographs*
Fracture surfaces were studied using a scanning electron microscope (type JSM by JEOL, Tokyo, Japan). Magnifications up to 10000 times were used.

2.2 Optical micrographs

Samples were imbedded in resin, and the surfaces were ground and polished. Prepared samples were examined with a photomicrographic apparatus (Panphot) furnished with a xenon lamp (Leitz, Wetzlar, Germany). Photomicrographs were taken with Polaroid 3000 film.

2.3 Transmission electron micrographs

Samples were prepared as thin fragments and mounted on a colloidon film supported by a copper mesh. Bright field images and selected area electron diffractions were examined under a Philips EM-300 microscope.

2.4 X-ray diffraction analyses

X-ray diffraction data were obtained using a Picker–Siemens or Norelco x-ray diffractometer with Ni-filtered Cu $K\alpha$ radiation. Interlayer spacings and average crystallite sizes were calculated by the Scherrer–Warren method, using the (002) diffraction line with silicon as an internal standard.

2.5 Densities

Densities of the polymers were measured using a methanol displacement method with a pyknometer. Densities could be measured within $\pm 0 \cdot 003$ g cm^{-3}. Densities of carbon samples were determined on powdered material, passing through -400 mesh, by a sink–float method using mixtures of chloroform or carbon tetrachloride and 1, 1, 2, 2-tetrabromoethane. These densities could be determined within $\pm 0 \cdot 02$ g cm^{-3}.

2.6 Infrared analyses

Infrared spectra of polymers and pyrolyzed samples were obtained using a Perkin–Elmer 621 grating infrared spectrophotometer. Established procedures were used in the preparation of KBr pellets containing 1 wt.% concentration of sample.

3 Results and discussion

3.1 Polymerization of divinylbenzene under pressure

It was found that pressure polymerization proceeded very rapidly without the use of catalyst and yielded hard non-porous pieces which were insoluble in common solvents. Densities, refractive indices, and infrared spectra are shown in figures 1–3. The results are compared with those for a polymer prepared at 1 atm and room temperature in the presence of the catalyst azobisisobutyronitrile. Densities and refractive indices of the polymers increased with increasing pressure. It is also noted that absorption by the vinyl functional groups at 985 and 1630 cm^{-1} decreased progressively with increasing polymerization pressure. An increase is observed in what is believed to be the absorption by a saturated isopropyl functional group at 1370 cm^{-1}. The observations are summarized in figure 4.
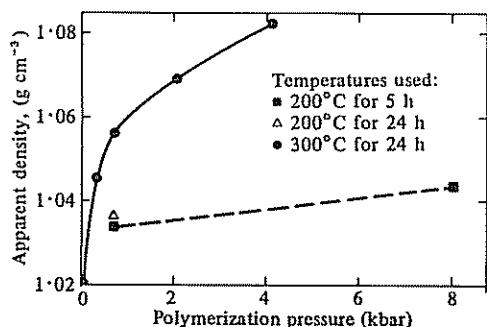

Figure 1. Change in density of DVB polymer with polymerization pressure.
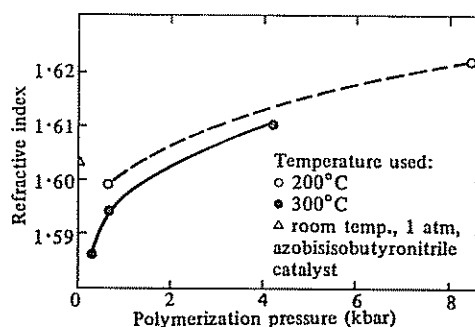
Figure 2. Refractive index of polymers of DVB prepared under pressure.

From the behavior of densities and refractive indices it is apparent that the most rapid increases occur at pressures up to about 1 kbar, but that increases continue up to at least 4 kbar polymerization pressure. Infrared data show, however, that above 1 kbar pressure ceases to have significant effect on the progress of polymerization and that, therefore, through the higher pressure range refractive indices and densities are probably influenced more by a decrease in macro- and microporosities than by a greater degree of saturated carbon–carbon linkages.

That the intimate structure of the polymer is nevertheless influenced through the full range of polymerization pressure is further demonstrated in subsequent carbonization.
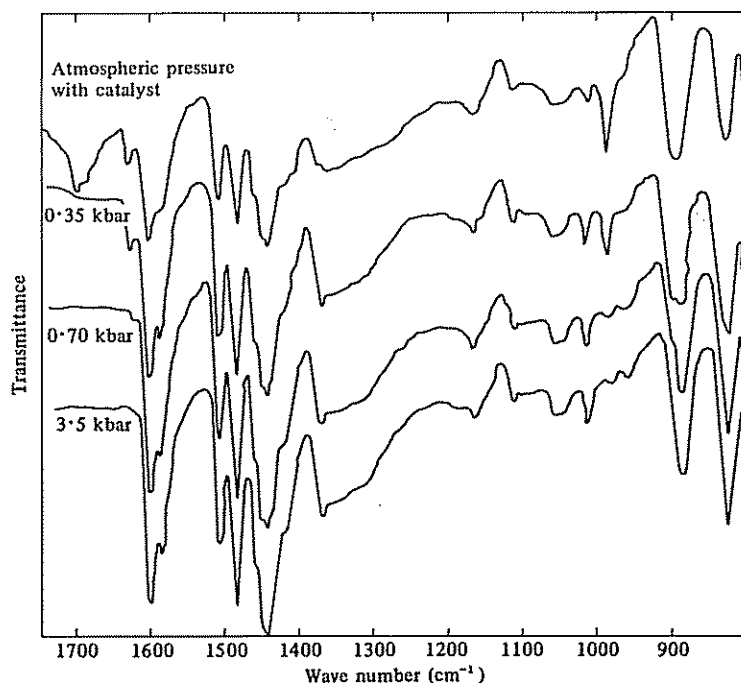

Figure 3. Portions of infrared absorption spectra of the catalyzed-room-temperature DVB polymer and of the polymers formed under pressure at 300°C.
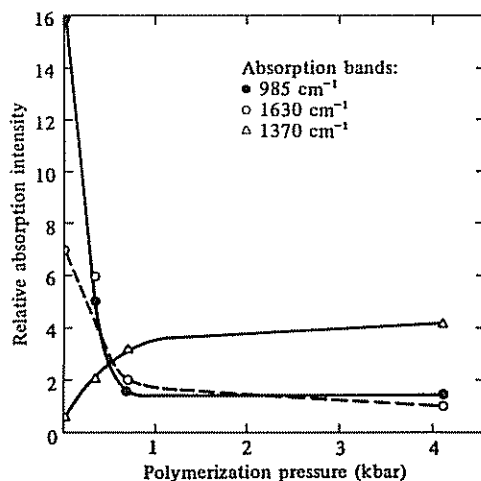

Figure 4. Change in intensities of absorption bands referred to in figure 3.

Figure 5 shows that the spherulite size of isotropic carbon formed under one set of carbonization conditions decreases steadily with increasing pressure of polymerization. It was also observed that the lower-pressure polymer could lead to the production of spherules which would coalesce in part.
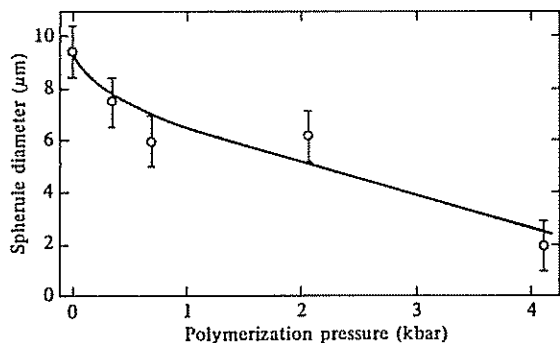

Figure 5. Variation in diameter of isotropic carbon spherulites produced by carbonization under 0·69 kbar pressure at 900°C and 3 h soak time following polymerization of DVB at various pressures.

3.2 *Pressure pyrolysis and carbonization of polydivinylbenzene*

The morphology of the carbons formed was remarkably affected by the carbonization pressure. Figure 6 outlines results of pressure pyrolysis of DVB, with reference to pressure and temperature of carbonization. Prior to carbonization, polymerization was conducted at 300°C and 0·69 kbar pressure. The figure is not an equilibrium diagram, because a soak time of 3 h was not sufficient to achieve equilibrium, but
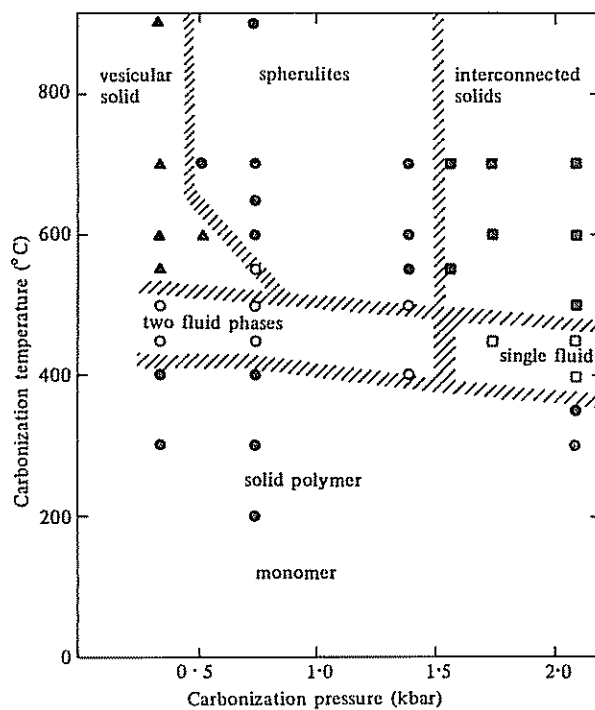

Figure 6. Quenched products from DVB related to the pressures and temperatures of carbonization. Treatment was in sealed gold capsules, heating to temperature at a standard rate of 6·5 K min^{-1}, and holding at temperature for 3 h.

it does serve to indicate the long-time trends of a closed reaction system. The figure indicates the relative stabilities of monomer and polymer in terms of pressure and temperature and also suggests the importance of surface energies in determining the phase separations in such pyrolyzing systems.

Carbonization between 400 and 500°C at pressures below 1·4 kbar led to an aggregate of products which segregated into two fluid phases. At least this is what is inferred from the quenched sample, where in the opened capsule was found a mixture of tar and wax. At pressures above about 1·4 kbar only a single isotropic 'glassy' phase was quenched.

At temperatures above 500°C the physical behavior of the carbonization products is interpreted as follows. Below about 0·48 kbar the viscosity of the carbonizing mass increases rapidly to form a continuous matrix which traps lower molecular weight gaseous components in irregular vesicles (figure 7a). Between 0·48 and 1·40 kbar
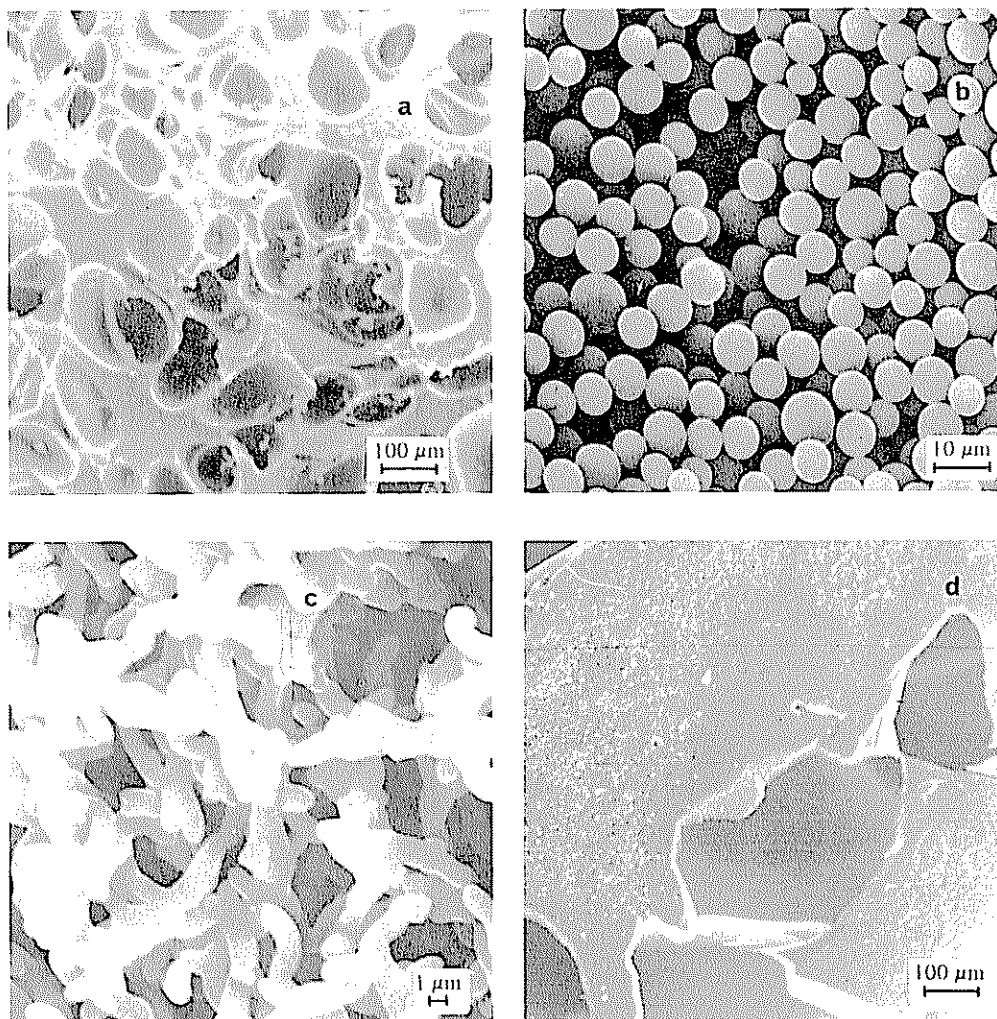

Figure 7. DVB polymer formed at 0·69 kbar and 300°C then carbonized at 700°C at a heating rate of 6·5 K min^{-1} under various pressures: (a) vesicular solid obtained under 0·48 kbar; (b) spherulites produced at 0·69 kbar; (c) interconnected solids produced at 2·07 kbar; (d) carbon obtained in nitrogen flow at 1 atm.

the carbon precursor is optically isotropic. In this range high-carbon high-molecular-weight components nucleate as liquid droplets in an increasingly fluid matrix. The droplets grow until they contain most of the carbon of the system, remaining suspended in the fluid matrix as they become more highly carbonized. During this time part of the fluid matrix is also carbonizing against the capsule wall. On quenching, the matrix further condenses onto the capsule walls, releasing gases and leaving free-standing spherulites of isotropic-carbon precursor (figure 7b). At pressures above 1·4 kbar fibrils of high molecular weight components nucleate and extend through the increasingly fluid matrix and tend to form at three-dimensional lattice-work. Here, too, the fluid matrix carbonizes and quenches against the capsule walls, leaving the carbonizing fibril lattice in a gaseous atmosphere (figure 7c). Carbon precursors of this type have an interconnected three-dimensional morphology which is a step toward forming what has been termed a periodic minimal surface by Donnay and Pawson (1969). That is, a solid is formed with is porous and permeable, with both the solid and pore spaces being continuous. The fibrils forming the lattice-work are of about one micron in diameter and are optically anisotropic. It appears that the effects of high pressures were combined with a high surface tension of the fibril surfaces to induce orientation effects in the fibrils, resulting in the final anisotropic character of the solid.

A major, but not unexpected, difference to be found in pressure carbonization is the high carbon yield of the order of 80% of the gross charge. This may be compared with the yield of only 8% after carbonizing the same kind of polymer in a conventional atmospheric-nitrogen flow. Figure 7d is a scanning electron microscope view of a carbon produced under atmospheric conditions. Note the irregular pores and grainy nature of the solid which is, however, optically isotropic.
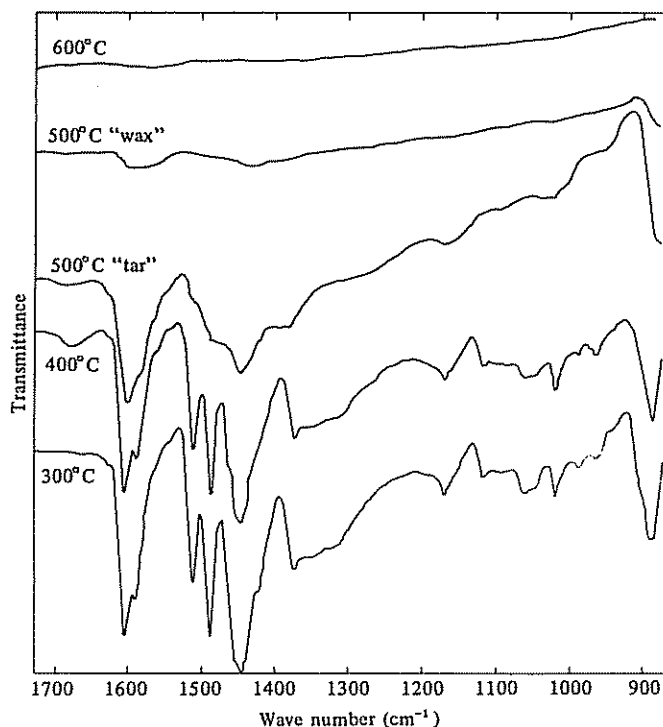

Figure 8. Change of infrared spectra with increase in carbonization temperature of PDVB under 0·69 kbar.

In figure 8 are illustrated the infrared spectra of various products formed during treatment under 0·69 kbar. The PDVB obtained at 300°C under pressure was transparent and of a pale yellow color. The polymer decomposed above 400°C, taking on a brownish color. After quenching from 500°C two substances were found inside the capsule. One was a wax-like substance, forming the bulk of the sample; and the other was a tar which wet or was frozen to the walls of the capsule. The wax-like material was made up of compounds of very high carbon content, and the tar of compounds of appreciable hydrogen content. This is evident from the infrared spectra.

Figure 9a shows a scanning electron micrograph of the wax-like substance produced at 500°C after extracting with benzene. As shown in figure 9b, nuclei of spherical structure first become noticeable at 600°C, and with time and increased temperature grow to form what is essentially an isotropic carbon precursor of the types shown in figures 9c and 9d. Associated with the spherical carbon was a small amount of isotropic flaky char which formed on the walls of the capsule. The carbon, which was
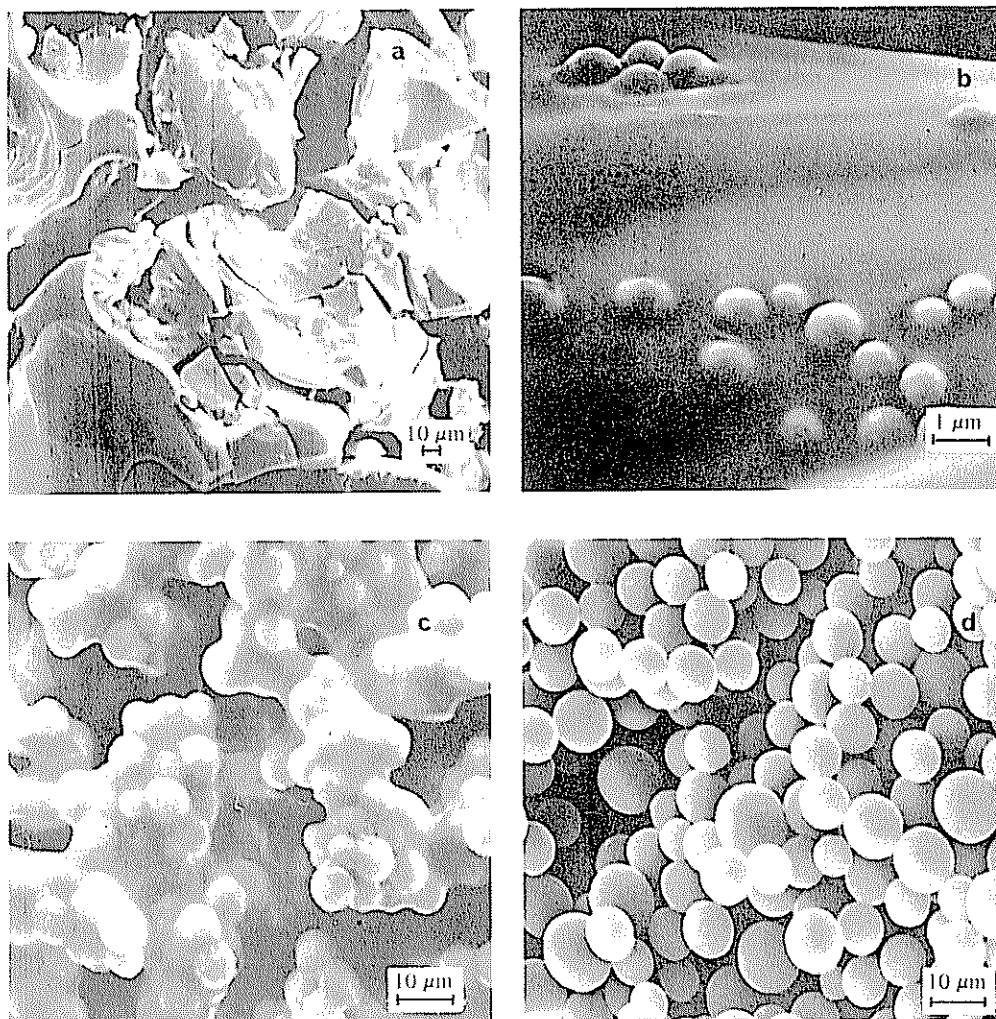

Figure 9. Progress of spherulitic carbon formation upon carbonization of PDVB at 0·69 kbar: (a) 500°C, 3 h; (b) 600°C, 3 h; (c) 650°C, no soak time; (d) 650°C, 3 h.

in the form of spherules 1 to 10 μm in diameter, was optically isotropic in polished sections. Some closed pores were evident inside the spherules. These isotropic spherulitic-carbon precursors were amorphous to x-ray and electron diffraction. Furthermore, selected-area electron diffraction did not reveal any three-dimensional crystallinity or preferred orientation but showed only diffuse diffraction rings.

The process of the formation of isotropic carbon spherulites is considered to be similar to that of the liquid-liquid microphase separation common in many glass-forming systems, with the exception that in carbonization the separation is not reversible. At this point it is of interest to note the decription by Whittaker and Grindstaff (1972) of isotropic 'coke ball' structure in commercial cokes formed from a California crude. The coke ball is made up of isotropic carbon spherules bound together with a relatively anisotropic carbon matrix, strongly indicative of the coexistence of at least two liquid substances during the coking process.

It was found in our work that the size of the isotropic carbon spherules was highly responsive to variables such as polymerization pressure, carbonization temperature and soak time, permeability of the capsule, and addition of vinyl ferrocene to DVB. The growth of the spherules was rapid and reached a maximum size in 60 and 15 min at 700 and 900°C, respectively (figure 10).
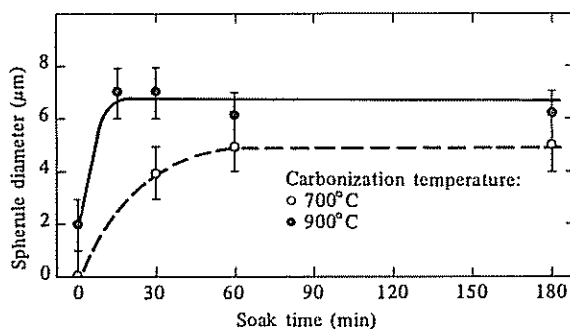

Figure 10. Growth of carbon spherulites from PDVB as a function of carbonization temperature and soak time. Carbonization pressure, 0·69 kbar.
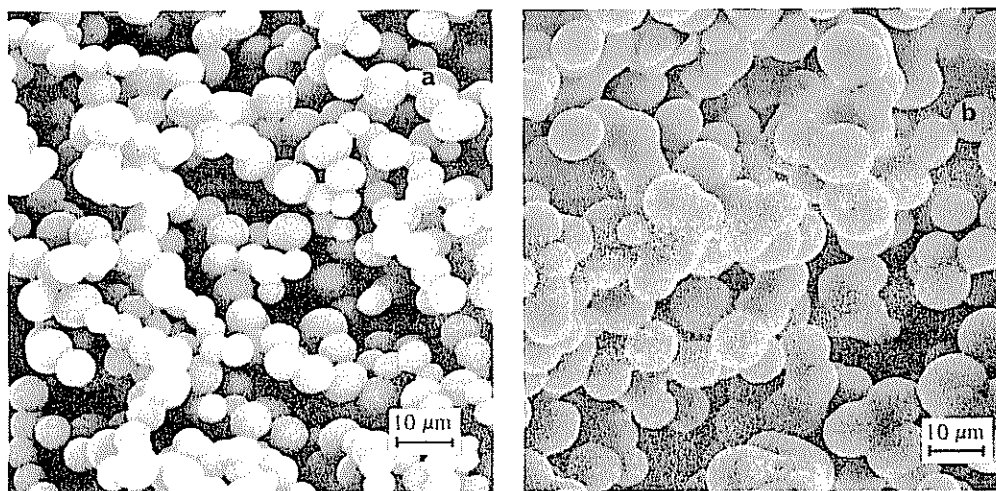

Figure 11. Effect of permeability of capsule material to hydrogen on size and coalescence of isotropic carbon spherulites produced from PDVB during carbonization to 900°C under 0·69 kbar: (a) in gold capsule; (b) in palladium-silver alloy capsule.

The permeability of the capsule to hydrogen also influenced the size and the coalescence of the carbon spherules, as shown in figures 11a and 11b. In a palladium-silver alloy capsule it was easier to obtain larger spherules and have them coalesce than in a gold capsule. The escape of hydrogen, one of the main pyrolytic products, through the sealed palladium–silver alloy capsule was confirmed by weight difference before and after an experiment, and the fact that after quenching the palladium–silver alloy capsule remained crushed, whereas the gold capsule was swollen by the pressure of residual product gases. With the escape of hydrogen during processing, the specific volume of the remaining sample decreased and thereby increased the possibility of contact between spherulites. Although no elemental analyses were made to support this view, it is reasonable to expect that loss of hydrogen from the palladium–silver capsules altered the total chemical composition enough so as to influence the chemical and physical behavior of the separating phases.
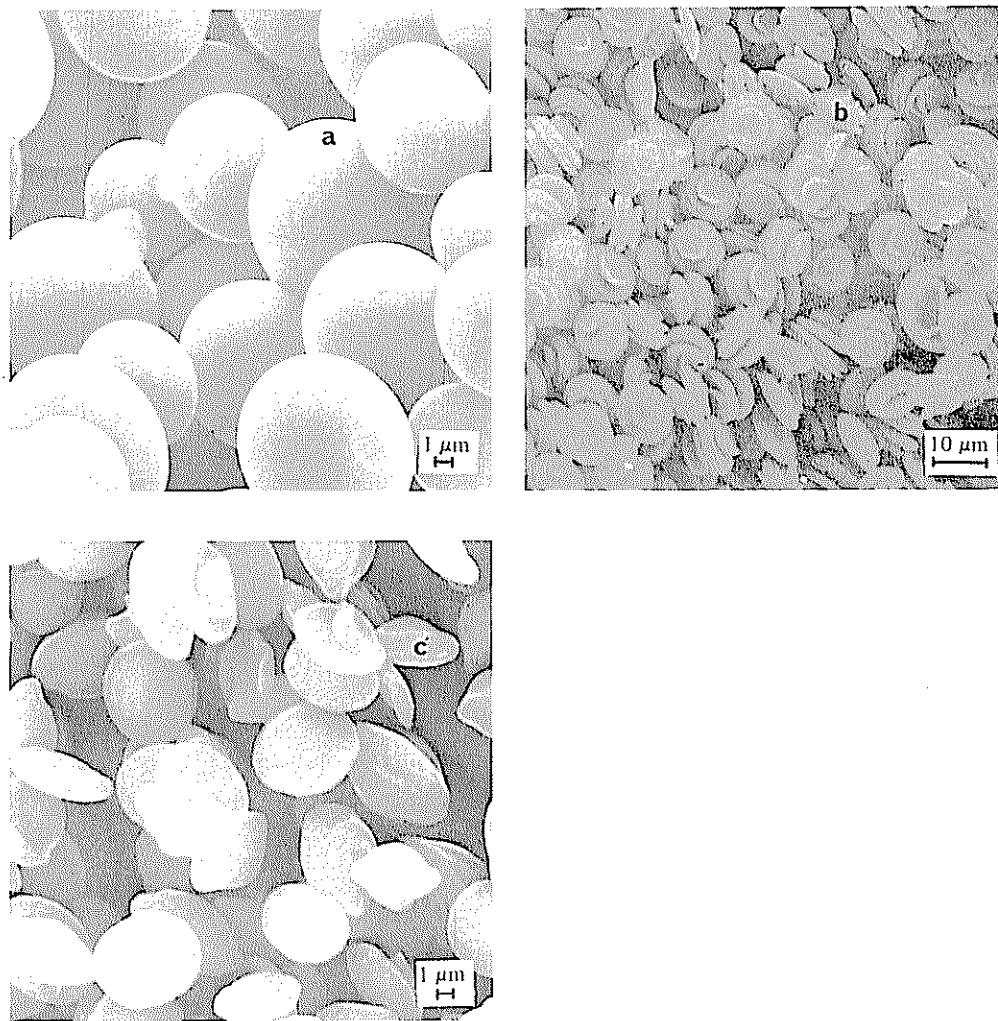
Figure 12. Scanning electron micrographs of carbons prepared: (a) from PDVB at 900°C under 0·69 kbar followed by heating to 2000°C in flowing helium; (b) from anthracene at 600°C under 1·7 kbar followed by heating to 2000°C in flowing helium; (c) from DVB +2wt.% vinylferrocene polymerized etc. as in (a).

Pressure carbonization at 700°C and 0·69 kbar of polymers containing 1–2% vinylferrocene resulted in spherulitic carbons of larger diameters than produced from pure DVB systems. For example, for preparations in palladium–silver capsules, additions of 1–2% vinylferrocene led to 10–12 μm diameter spherules compared with 3–5 μm spherules obtained from DVB alone. The use of as much as 10% vinylferrocene interfered with spherulite formation, resulting instead in irregularly shaped and fused fragments.

3.3 *High-temperature heat treatment*

A suite of carbons prepared from DVB was heat treated at temperatures up to 2200°C in flowing helium at atmospheric pressure. Figure 12a is a scanning electron micrograph of the spherulitic carbon prepared at 900°C under 0·69 kbar and then heat treated at 2000°C. Carbon spherules prepared under various conditions from DVB remained spherical and optically isotropic after heat treatment up to 2200°C, with only about a 3% decrease in diameter. This behavior may be compared with that of the anisotropic mesophase-carbon precursors obtained by the carbonization of anthracene under pressure. When these anisotropic spherulites are heated to 2000–2200°C, extensive cracking results, as shown in figure 12b.

Electron diffraction studies of the isotropic spherulitic carbon did not reveal any three-dimensional crystallinity. On the other hand, the carbon precursors (which were isotropic spherulites) formulated with 2% vinylferrocene underwent remarkable changes in particle morphology upon heat treatment at 2000°C, as shown in figure 12c. Not only did the carbon become optically anisotropic, but it also developed a very definite three-dimensional crystallinity as revealed by electron diffraction (see figure 13). The result was not unexpected, because of the well known catalytic effect of iron on the graphitization of carbon (Oberlin *et al.*, 1969; Albert, 1969).

Typical (002) x-ray diffraction line patterns of the carbon precursors from DVB and the 2000°C sample are shown in figure 14a. These diffraction maxima are broader and located at lower angles than those from carbons prepared from anthracene under similar conditions. The latter patterns are shown in figure 14b for comparison. The interlayer spacing and the average crystallite height L_c of the glassy-carbon precursors were about 3·58 and 14Å, respectively. Figure 15 shows the changes in the interlayer spacing and L_c with carbonization pressure for carbon precursors held at 700°C for 3 h and then heat treated at 2200°C for 3 h. The interlayer spacings on the carbons obtained under pressures lower than 1·6 kbar were about 3·44 Å, while

Figure 13. Selected-area electron diffraction pattern of the carbon shown in figure 12(c).

the carbons produced under higher pressures had an interlayer spacing of about $3 \cdot 40$ Å. The lower interlayer spacing is a direct consequence of the preferred orientation noticeable in the carbons produced from precursors prepared at pressures above $1 \cdot 6$ kbar. Such a definite discontinuity was also observed in the change of L_c with pressure, as shown in figure 15. This discontinuous boundary for the x-ray crystallographic parameters reflects the pressure–temperature region shown in figure 6 at which the isotropic or anisotropic carbons were formed, depending on the carbonization pressure.

Densities of the spherulitic-carbon precursors were about $1 \cdot 68$ g cm^{-3}; they increased to $1 \cdot 79$ g cm^{-3} on heating to 2000^{6}C. By comparison, 2000°C carbons from precursors prepared by polymerization and carbonization at atmospheric pressure had a density of about $1 \cdot 46$ g cm^{-3}. This result indicates that the use of pressure can result in an increase of density of the carbons prepared over standard preparations. However, a clear relationship between density and carbonization pressure was not obvious. A lack of correlation may arise, in part, because of the difficulties in measuring accurate densities of any material with closed pores by displacement methods, and the general limitations of the x-ray method when applied to materials of low crystallinity.

4 Conclusions

The effect of pressure on the polymerization and carbonization of DVB has been studied, with regard to variables such as temperature and soak time, the permeability of sealed capsules to hydrogen, and the addition of an organometallic compound. Pressure polymerization proceeded rapidly at 300°C without the use of a catalyst
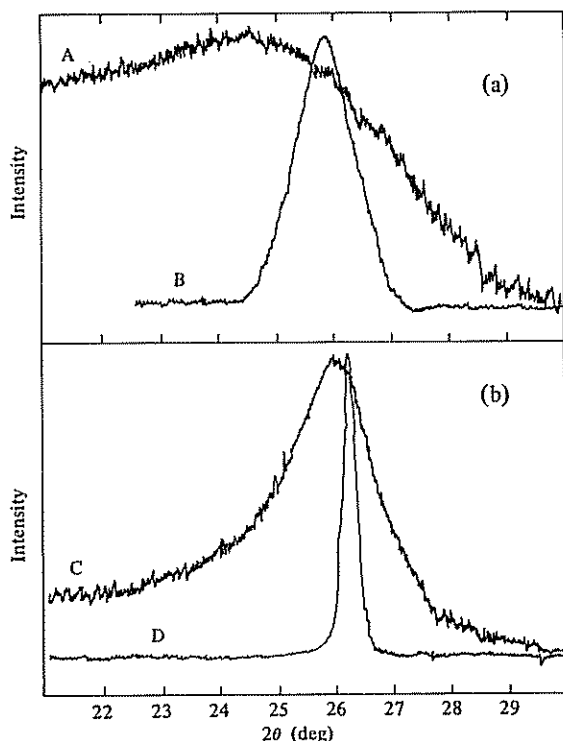

Figure 14. Typical (002) x-ray diffraction patterns: (a) DVB after pressure polymerization and pressure carbonization to 900°C at $0 \cdot 69$ kbar for 3 h (curve A) followed by atmospheric pressure heating at 2000°C for 3 h (curve B); (b) anthracene carbonized under 1 kbar at 600°C for 1 h (curve C) followed by atmospheric pressure heating at 2000°C for 3 h (curve D).

and yielded hard non-porous dense pieces which were insoluble in common solvents. It was also found that the morphology of the carbon was remarkably affected by the carbonization pressure. This result suggests the probability of producing carbons of a different morphology by the use of pressure.

Relationships found between morphology and pressure–temperature conditions for a chemical system starting with a DVB polymer may serve as a model for some other polymers or copolymers of the same kind, hopefully with the pressure–temperature areas displaced downward to more practical values from the industrial point of view. Our experience with polymerized furfuryl alcohol has so far shown that it does not follow the morphological patterns of PDVB, although it, too, yields ultimately a glassy carbon.

Among the most interesting results are the occurrences of the optically-isotropic spherulites and the slightly-anisotropic interconnected solid structure which approaches a periodic minimal surface. It might be possible, by a careful selection of processing variables, to produce carbon in a series of morphologies extending from a mass of free spherulites to slightly or extensively sintered spherulites, to complexly joined rods, to interconnected solids, and on to an ideal periodic minimal surface. When endowed with a controlled microporosity, the resulting carbons may find uses in many areas of catalysis, molecular sieves, and adsorption.

The special morphologies obtained with the use of pressure in the early stages of carbonization have their origins in the nucleation of the discontinuous liquid phase of two immiscible liquids formed from the confined pyrolytic products. It is believed that the nucleation density under certain conditions determines the final morphology. Further study would be necessary to follow the details of nucleation and growth leading to the observed carbon microstructures.
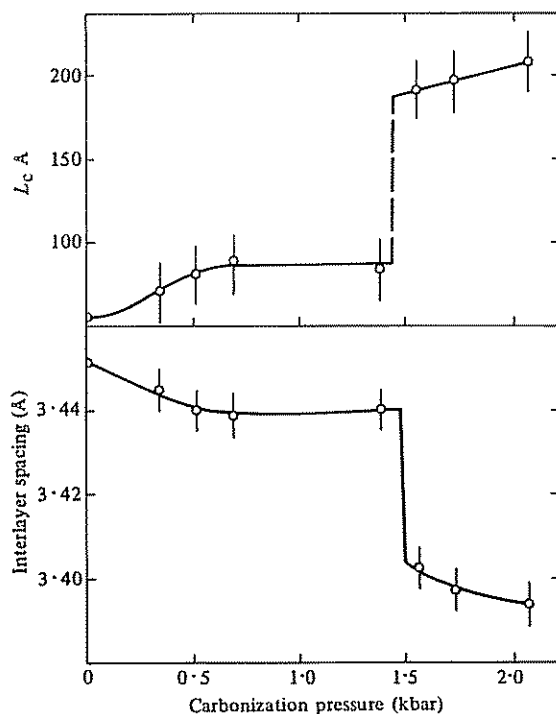

Figure 15. Effect of carbonization pressure at 700°C on the interlayer spacing and average crystallite height L_c of carbons which were subsequently heated to 2200°C at atmospheric pressure.

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