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Formation of non-graphitizable isotropic spherulitic carbon from poly-divinylbenzene by pressure pyrolysis

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Isotropic spherulites of carbon stable at 2000° C were synthesized by the pressure pyrolysis of divinylbenzene polymer sealed in a capsule. The morphology of the synthesized carbon was pressure and temperature dependent being influenced by the state of polymerization of the starting polymer. Using a polymer prepared at atmospheric pressure and 150° C without catalyst, isolated spherulitic carbon was formed at 700° C and pressures of 1000 to 1250 kg cm^{-2}. These spherulitic carbons were optically isotropic, hard and non-graphitizable after heat treatment at 2000° C. Such carbons originate in the co-existence of higher and lower molecular weight products of pressure pyrolysis and the survival cross-linkages in the original polymer.

1. Introduction

Many kinds of organic compounds have been pyrolysed to carbon with desired properties. The graphitizability of resultant carbons depends markedly on the original organic compound. Kipling *et al.* [1] reported that graphitizable carbons are produced only when an organic compound fuses during carbonization. Brooks and Taylor [2] described the formation of mesophase in the carbonization of the coal-tar pitch. Since then, attention has been directed to the importance of the formation and the coalescence of mesophase, which leads to the anisotropic optical texture of graphitizable carbon.

Pressure influences solubility, viscosity, density, and phase separation of mesophase polymerization and pyrolysis, as well as the graphitizability of resultant carbons [3–6]. Hirano *et al.* [7] observed the formation of isotropic carbon by carbonization under pressure.

Divinylbenzene (DVB) can form a thermosetting polymer. This paper describes the formation of isotropic non-graphitizable carbon spherulites stable at 2000° C by the pressure pyrolysis of DVB.

2. Experimental details

As the starting material a mixture of 55% *m*- and *p*-divinylbenzene and 45% ethyvinylbenzene was polymerized at 300° C for 2 h under 1000 kg cm^{-2} (about 100 MPa) or at 150° C for 30 min under atmospheric pressure without catalyst. Differential thermal analysis (DTA) of the mixture sealed in a gold capsule showed that polymerization began at 150° C.

All pressure work was carried out in a hydrothermal apparatus of the cold-seal type. The polymer samples were sealed in thin-walled gold capsules of 3.0 to 7.0 mm diameter and 50 mm length. The sample polymerized at atmospheric pressure was < 1 mm in size so as to set in a capsule. Pyrolysis of polymers was carried out at selected temperatures up to 800° C under pressures up to 2000 kg cm^{-2} (about 200 MPa). Pressure was measured with a Heise gauge and temperature was controlled with a sheathed thermocouple set in the pressure vessel. The temperature was raised at 10° C min^{-1} and quenched after an experimental run. The carbon specimens produced were further heat-treated at 2000° C for 1 h in a flow of argon.

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The carbons produced were characterized by X-ray diffraction and scanning electron microscopy and polarized light microscopy. The density of the carbons was determined within ± 0.02 g cm^{-3} by a sink–float method using mixtures of acetone and carbon tetrachloride. The products of pyrolysis were analysed by infra-red spectroscopy and gel-permeation chromatography (GPC) on the quenced sample in the gold capsule.

3. Results and discussion

3.1. Morphology of carbons formed by pressure pyrolysis

Pressure polymerization proceeded very rapidly without the use of a catalyst and yielded hard non-porous pale-yellowish pieces which were insoluble in common solvents and contained residual vinyl functional groups. The solid polymer synthesized at atmospheric pressure showed stronger infra-red absorption by vinyl groups (factor of 5).

The morphology of resultant carbon depended strongly on the pressure and temperature of pyrolysis and the nature of polymerization within the polymer.

A porous carbon (Fig. 1a) was formed under pressures below 1000 kg cm^{-2} at 615° C. Coalescing carbon spherulites were found at pressures above 1300 kg cm^{-2} (Fig. 1b) at 615° C. Between 1000 and 1300 kg cm^{-2}, the carbon specimen consisted of mixtures of porous carbon and coalescing carbon spherulites. The pore size in the porous carbon decreased with increasing pyrolysis pressure, from 35 to 50 μm at 700 kg cm^{-2} to 10 to 30 μm at 1100 kg cm^{-2} at 615° C. The bulk density of the porous carbon was 0.95 to 1.05 g cm^{-3}. Isolated carbon spherulites were obtained at 1100 kg cm^{-2} at 700° C and also at 1300 kg cm^{-2} at 750° C. Individual carbon spherulites (Fig. 1c) could be synthesized at 1000 to 1250 kg cm^{-2} and between 660 and 700° C, using polymers prepared at atmospheric pressure. The diameter of the carbon spherulite was 3 to 10 μm with a density of 1.55 to 1.57 g cm^{-3}. The spherulites coalesced during pressure pyrolysis above 1500 kg cm^{-2}. Fig. 2 summarizes the conditions for formation of several morphologies of resultant carbon. Soak times of 3 h were used.

The carbon specimens synthesized in this study were optically isotropic.

Important effects in pressure pyrolysis are the high carbon yield of the order of 80% of the charged polymer as compared with about 10% by pyrolysis of the same polymer in nitrogen, as well as the possibility of control over the morphology of the carbons.

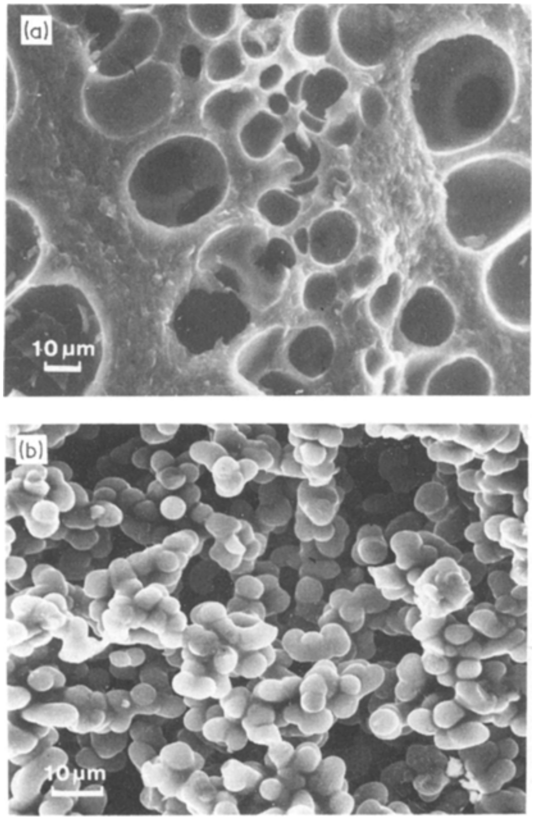
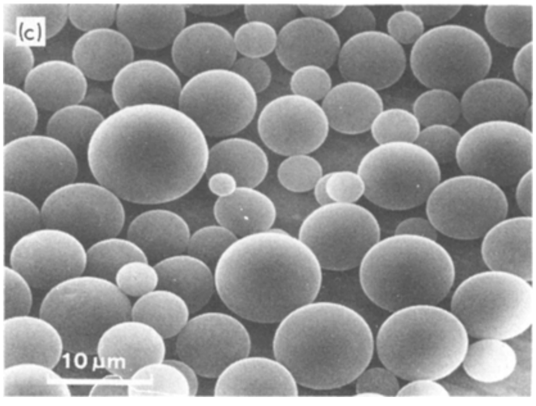


Figure 1 Morphology of carbons formed by pressure pyrolysis of polydivinylbenzene. (a) Porous carbon formed by pyrolysis at 615° C and 900 kg cm^{-2} of a polymer prepared at 1000 kg cm^{-2}. (b) Coalescing carbon spherulites formed by pyrolysis at 615° C and 1300 kg cm^{-2} of a polymer prepared at 1000 kg cm^{-2}. (c) Spherulitic carbons formed by pyrolysis at 700° C and 1000 kg cm^{-2} of a polymer prepared at atmospheric pressure.



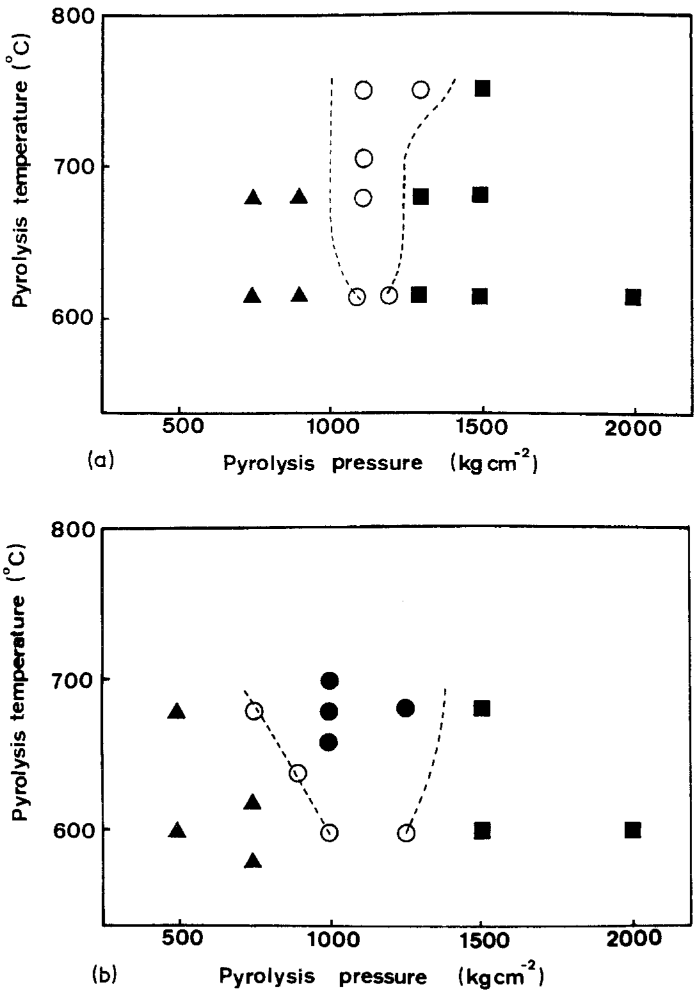


Figure 2 Formation of carbons with various morphologies on pressure pyrolysis of polymer prepared at (a) 300° C and 1000 kg cm^{-2} for 2 h and (b) 150° C at atmospheric pressure for 30 min. ▲; porous carbon, ●; spherulitic carbon, ■; coalescing spherulitic carbon, ○; mixture of porous carbon and coalescing spherulitic carbon.

These spherulitic carbons retained their morphology and isotropy after heat treatment to 2000° C, with a weight loss of about 7%. The spherical shape does not change on heat treatment (Fig. 3) unlike the anisotropic spheres which show extensive cracking [6]. Fig. 4 shows the X-ray diffractions on the carbon spherulites, of heat treatment temperatures at 700 and 2000° C. Crystallite heights increased on heat treatment to 2000° C to 12 nm. The interlayer spacing was 344 pm at 2000° C. The average number of layers in the crystallite is 30 to 40.

3.2. Process of formation of non-graphitizable isotropic carbon spherulites

The isotropy and non-graphitizable properties of the carbon spherulites are attributable to the "disordered" bonding of the polymer. The following spectroscopic changes were observed. (1) at about 410° C, the vinyl functional group of the original polymer disappeared, (2) there was a decrease in the number of methylene groups from

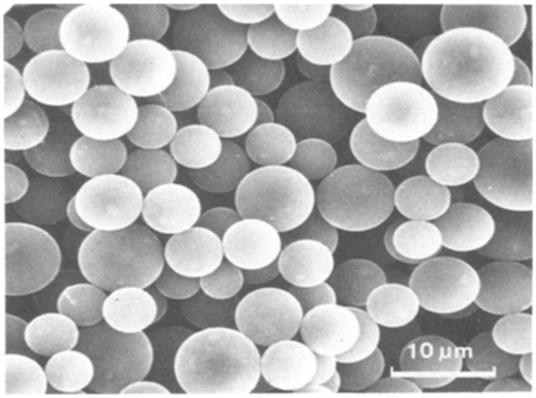


Figure 3 Photograph of carbon spherulites after heat treatment at 2000° C in Ar of the specimen shown in Fig. 1c.

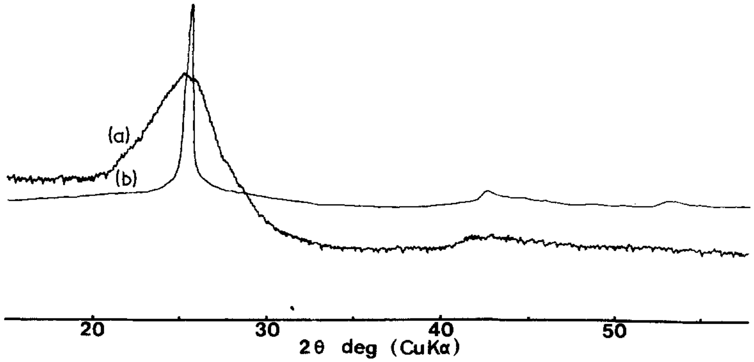


Figure 4 X-ray diffraction of spherulitic carbons before and after heat treatment at 2000° C for 1 h. (a) Original spherulitic carbons before heating. (b) Carbon after heating to 2000° C.

410° C to about 580° C, (3) meta(*m*)- and para(*p*)-disubstituted benzene rings (different from the original polymer) appeared above 440° C, (4) an increase occurred in the number of ortho(*o*)-disubstituted benzene rings.

The *m*- and *p*-disubstituted benzene rings formed just after the decomposition of the original polymer (Fig. 5a) were from lower molecular weight material (Fig. 5b). The *o*-disubstituted benzene rings formed at the later stages of thermal decomposition and then gradually increased so leading to condensed aromatic rings and the development of a turbostratic structure. The survival of carbon–carbon cross-linkages in the original polymer even at 580° C, in carbon spherulites prevents the development of large two-dimensional graphitic layers. Fig. 5c models schematically a structure for the isotropic, turbostratic non-graphitizable carbon from DVB.

This model suggests that the polymer begins to decompose above 410° C and becomes brownish in colour. A homogeneous fluid is formed with molecular weights less than 5000 at 440° C. At 530° C, a wax-like material co-exists in the fluid matrix. The wax-like substance was made up of components of molecular weight above 10 000 amu

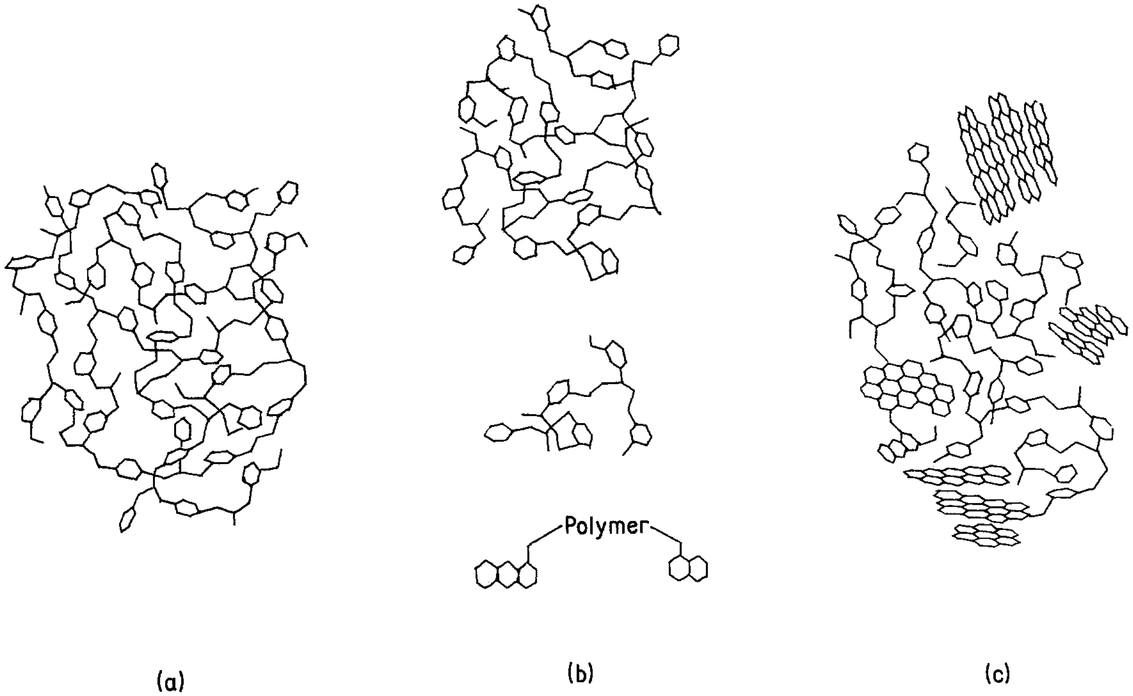


Figure 5 Structural changes in pressure pyrolysis of polydivinylbenzene. (a) Original polymer, (b) intermediate state (phase separation of pyrolysis liquid, (c) carbon formed.

which cause the increase in the number of *o*-substrated benzene ring. It appears probable that the liquid–liquid microphase separation must be of importance for the formation of the carbon spherulites. The high molecular weight components nucleate as liquid droplets in the fluid matrix. The droplets grow, remaining suspended in the fluid matrix as the pyrolysis continues. The phenomenon of irreversible spherulitic carbon formation may be similar to reversible microphase separation in spinoidal decomposition in glass-forming systems.

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