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Carbonization and graphitization of poly-*p*-phenylene sulphide (PPS) film

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Oriented poly-*p*-phenylene sulphide (PPS) films (thickness 12 and 75 μm) and PPS powder were carbonized/graphitized after stabilizing by oxidation, in order to examine the effect of sulphur on graphitizability of the resulting carbons. The films and the powder resulted in carbons with a high and a low graphitizability respectively. An "in-plane oriented structure" of the PPS film was the most predominant factor to lead to a high graphitizability, and sulphur in the precursor did not lower the graphitizability when it was subjected to solid-phase carbonization. These phenomena are discussed on the basis of analytical data.

1. Introduction

It is known that solid-phase carbonization results in a non-graphitizing carbon. Recently, a highly crystallized graphite film was prepared through solid-phase carbonization of polymers with a preferred orientation of constituent molecules [1–3]. Many of these polymers contained nitrogen in their structures, but the behaviour of nitrogen in the carbonization process, especially with respect to graphitizability of the resulting carbon, has been scarcely discussed.

Sulphur is also an important constituent element for polymers. Sulphur added to pitch material accelerates a liquid-phase carbonization process, resulting in cross-linkage between constituent molecules, and lowers the graphitizability of the resulting carbon [4, 5]. Sulphur incorporated in an aromatic ring system remains up to a high temperature and acts as a graphitization catalyst ca. 1700 °C to accelerate the graphitization process [6]. However, the literature contains little about the graphitizability of an oriented sulphur-containing polymer after solid-phase carbonization. The present paper reports on carbonization and graphitization behaviours of a poly-*p*-phenylene sulphide (PPS) film with an "in-plane orientation".

2. Experimental procedure

2.1. Materials

Biaxially stretched PPS $[\{C_6H_4\text{–}S\}n]$ films (Trade name Torerina) of 12 and 75 μm thickness were supplied by Toray Co. The number-average and the weight-average molecular weights of this PPS were ca. 10 000 and 50 000, respectively. One wt % of additive was contained in the PPS to improve lubricity of the film. PPS powder, No. E1880 (Toray Co.), was used as reference.

2.2. Heat-treatments

Since as-received PPS film fused by heating, the film with fixing edges (20 × 20 mm) was stabilized in an oxygen stream as follows: room temperature $\rightarrow$ (1 °C min^{-1}) $\rightarrow$ 280 °C (held for 10 h) $\rightarrow$ (1 °C min^{-1}) $\rightarrow$ 310 °C (held for 5 h) $\rightarrow$ (1 °C min^{-1}) $\rightarrow$ 325 °C (held for 5 h). The film colour changed from pale brown to dark red–brown after stabilization. The film without fixing shrank somewhat after this treatment. The PPS power was also stabilized in the same way.

The stabilized samples were carbonized at prefixed temperatures between 400 and 1200 °C in a nitrogen stream. The heating rate and the holding time were 5 °C min^{-1} and 1 h, respectively. Part of the sample, after carbonization at 1200 °C was further heated at 1400, 2000 and 3000 °C under an argon stream. The heating rate and the holding time were 20 °C min^{-1} and 10 min, respectively.

2.3. Measurements

TG/DTG measurements were carried out with a heating rate of 5 °C min^{-1} in a nitrogen stream. Contents (wt %) of S and C were measured by a combustion method using tin particles as a combustion accelerator. The KBr-tablet method was used for i.r. spectral measurements. Gases evolved from the film by heating were determined by use of GC/mass spectroscopy. A preferred orientation of the film was determined by X-ray diffraction using CuKα radiation. A degree of graphitization was determined by Raman spectroscopy.

3. Results

3.1. TG/DTG

Fig. 1 shows TG and DTG curves of the PPS film. A remarkable weight loss of ca. 40% occurred between ca. 500 and 600 °C. At higher temperatures a slight weight loss continued.

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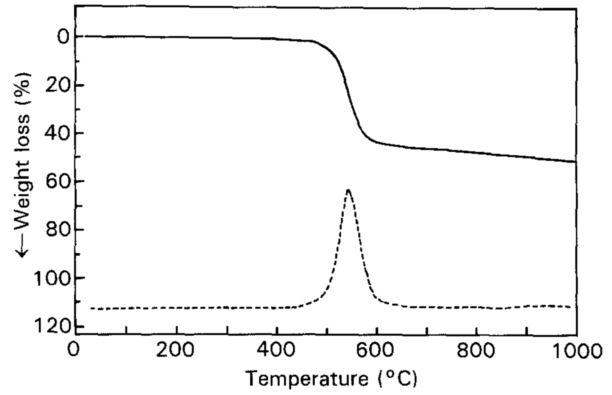

Figure 1 TG (—) and DTG (– – –) curves of the PPS film.

3.2. S and C contents

Fig. 2 shows changes in the S and the C contents in the film. The S and C contents in raw film corresponded well to the structure of $-\!\left(C_6H_6{-}S\right)\!-$. No change was observed up to 400 °C. With increasing temperature, the S content decreased and the C content increased. The molar ratio of S : C decreased to 1 : 83 after heating to 1200 °C. The behaviours shown in Figs 1 and 2 did not coincide with each other, which may have been the result of different heating conditions.

3.3. I.r. spectra

The i.r. spectra are shown in Fig. 3. Note the absorptions of δ (C–H) (two adjacent hydrogen atoms on the benzene ring) at 810 cm^{-1} and δ(C–H) (five adjacent hydrogen atoms on the benzene ring) at 740 and 710 cm^{-1}. δ(C–H) absorptions at 740 and 710 cm^{-1} became relatively stronger than the absorption at 810 cm^{-1}, indicating an increase in a phenyl end group.

3.4. GC/mass spectroscopy

The results of GC/mass spectroscopy are shown in Fig. 4. H_2S, H_2, CH_4 and benzene were important molecules in speculating the thermal degradation mechanism, but were not analysed in the present work. Almost no gases evolved below 450 °C. Volatile materials with low molecular weights, such as C_6H_6SH, evolved at 500 °C. With the rise of temperature, the composition of the evolved gases became very complex. The sulphur-containing aromatic compounds (⑤, ⑨) formed together with the compounds formed by breaking of the main chain of the PPS molecule (①–④, ⑥–⑧).

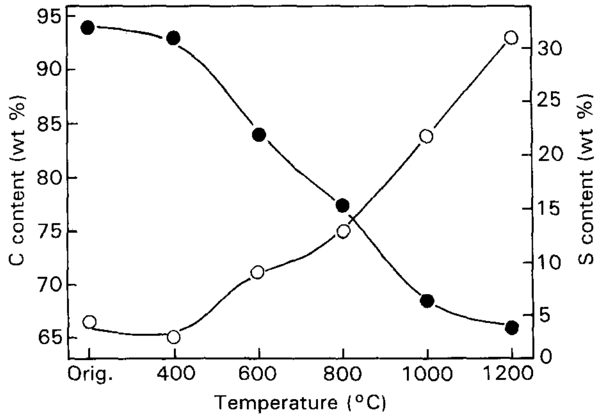

Figure 2 Changes of S (●) and C (○) contents in the PPS films with heating temperature.

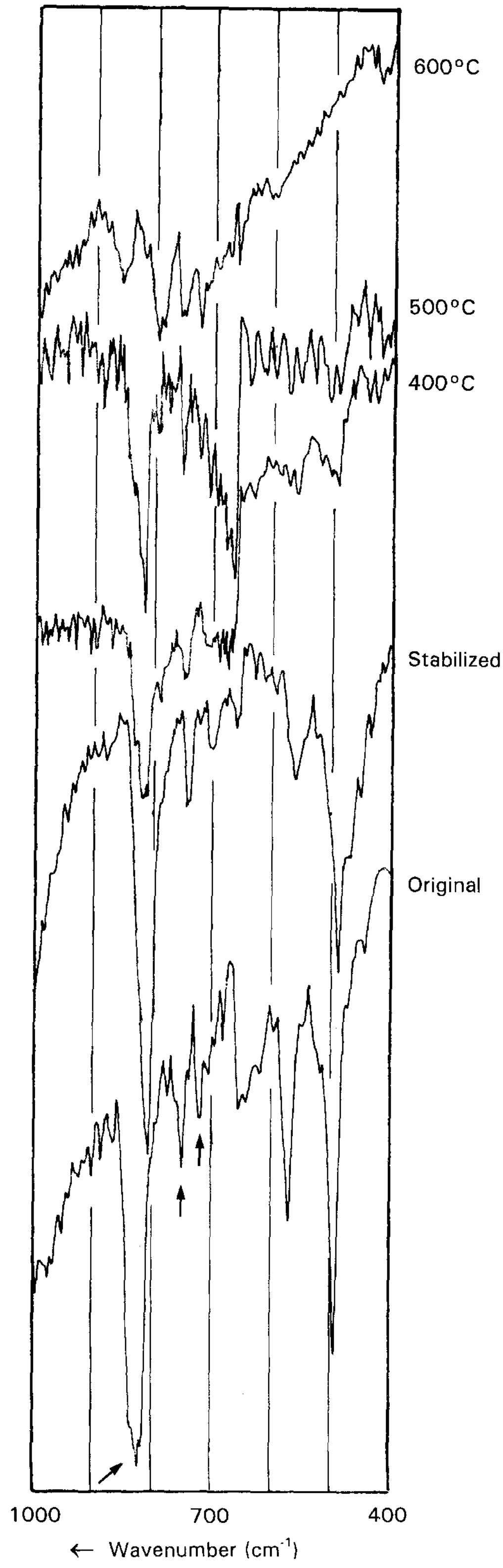

Figure 3 Changes in the i.r. spectra of the PPS films with heating temperature.

The atomic ratio of H in the evolved gases, on average, was larger than that of $\{C_6H_4S\}$, which meant the occurrence of dehydrogenation resulting in larger aromatic compounds.

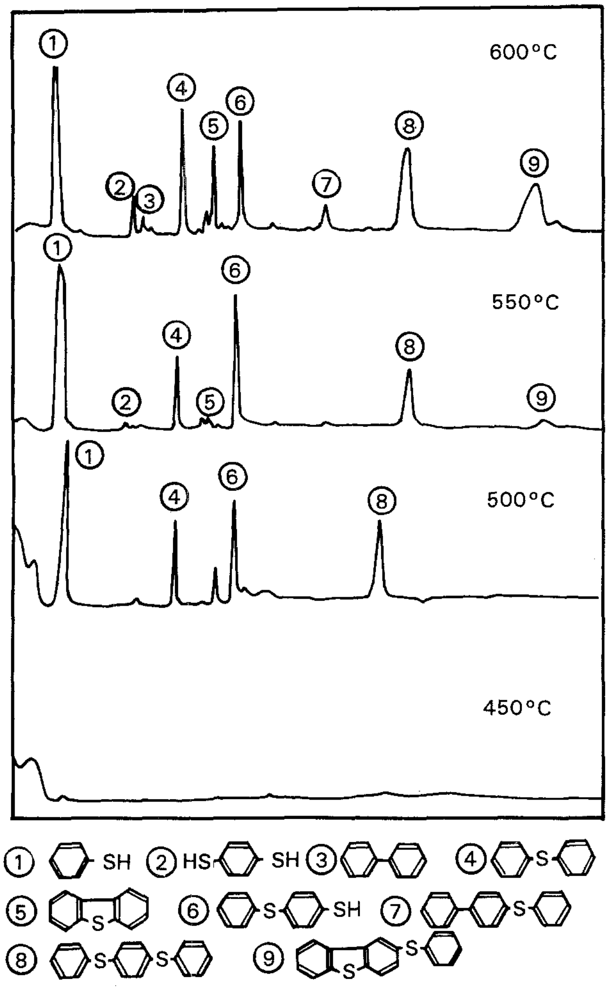

Figure 4 GC/mass spectroscopy spectra of gases evolved from the PPS film at various heating temperatures.

3.5. X-ray diffraction

PPS is known to have an orthorhombic unit cell ($a = 0.867$ nm, $b = 0.561$ nm, $c = 0.26$ nm) [7]. As stated above, this film was stretched biaxially to have a preferred orientation of the linear PPS molecule along the film surface (in-plane orientation). These data were confirmed in this work by use of X-ray diffraction, though not shown here.

3.6. Raman spectra

Fig. 5 shows change of Raman spectra of the 75 μm film with increasing temperature. The absorption at 1360 cm^{-1} weakened with the rise in temperature, and was scarcely observable in the sample after graphitization at 3000 °C. The absorption at 1580 cm^{-1} became sharper. Fig. 6 shows Raman spectra of the 12 and 75 μm films and the powder after graphitization at 3000 °C. Both films showed strong absorptions at 1580 cm^{-1} and almost no absorption at 1360 cm^{-1}. The powder sample gave an absorption at 1360 cm^{-1} together with a broad absorption at 1580 cm^{-1}. These results indicate that the film had a higher graphitizability than that of the powder sample [8].

4. Discussion

The linear PPS molecule has an in-plane orientation. Raman spectra (Fig. 6) clearly showed a higher graphitizability of the film sample than that of the powder sample. It is concluded that such a high graphitizability of the film resulted from an in-plane orientation of the PPS molecules in the film.

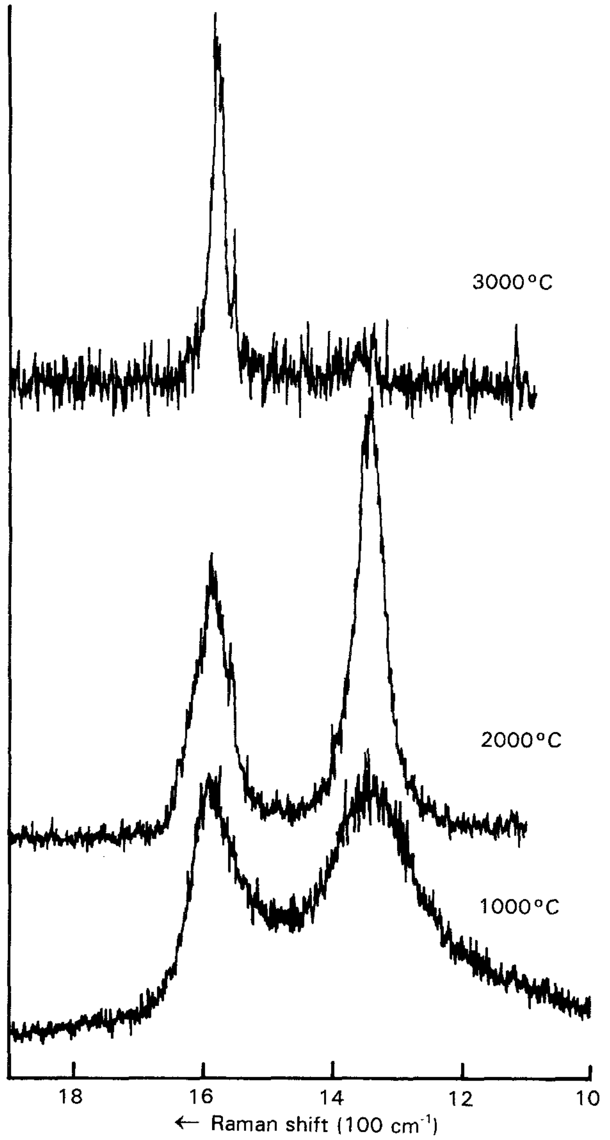

Figure 5 Changes in the Raman spectra of the 75 μm PPS film with heating temperature.

Weight loss and the S:C ratio were unchanged by the stabilization process. The structural change was not elucidated by i.r. spectroscopy. However, the colour change of the film (from pale brown to dark red–brown), implied that growth of the PPS molecules into a larger aromatic molecule must have occurred during the stabilization process. The structural change was also supported by shrinkage of the film, without fixing, after stabilization, though further details are not clear. The most important point is that the in-plane orientation of the film remained after stabilization.

The remarkable structural changes occurred at an initial carbonization process between 500 and 600 °C, as shown by: 1. TG and DTG curves, shown in Fig. 1; 2. a marked lowering of the S:C ratio, shown in Fig. 2; and 3. a clear change in the i.r. spectra, shown in Fig. 3. Ehlers *et al.* [9] reported that H_2S was a predominant gas at 450 °C, and H_2 at 550 and 620 °C. They also observed the formation of small amounts of methane

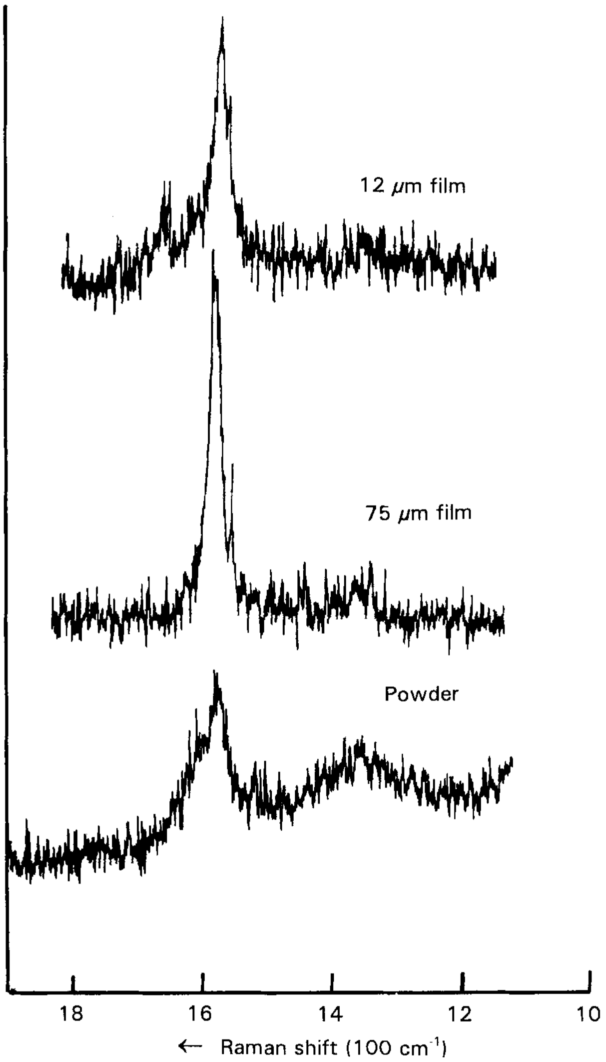

Figure 6 Raman spectra of the PPS films and the PPS powder after graphitization at 3000 °C.

and benzene. The formation of methane meant that fission of an aromatic ring had occurred. The serious structural changes of the PPS are suggested in the present work. The lowering of the S : C ratio, shown in Fig. 2, is thought to be caused mainly by H_2S evolution. Fig. 7 shows the formation mechanisms of the evolved gases, based on information from Figs 2–4 and X-ray diffraction data. Phenyl radicals formed in abundance in the initial carbonization process. Some of the radicals combined as shown in Fig. 7, but, simultaneously, others partook in intermolecular bonding to form the larger aromatic molecules. It should be emphasized again, the resulting aromatic molecules retained their in-plane orientation after carbonization, in so far as they did not fuse. An in-plane oriented structure is well-known to be favourable to "grow" graphite crystals on heating to high temperatures [1–3].

As described above, sulphur in a polymer with an in-plane orientation does not lower the graphitizability of the derived carbon when carbonized through the solid-phase, even after serious thermal degradation. Rather, sulphur acts to proceed the solid-phase carbonization favourably by forming cross-linkages [4, 5]. It is concluded, therefore, that a carbon precursor, with an in-plane orientation, is carbonized through the solid-phase, resulting in a graphitizing carbon, regardless of whether sulphur is contained in it or not. This idea will be extended to a carbon precursor containing nitrogen [1–3].

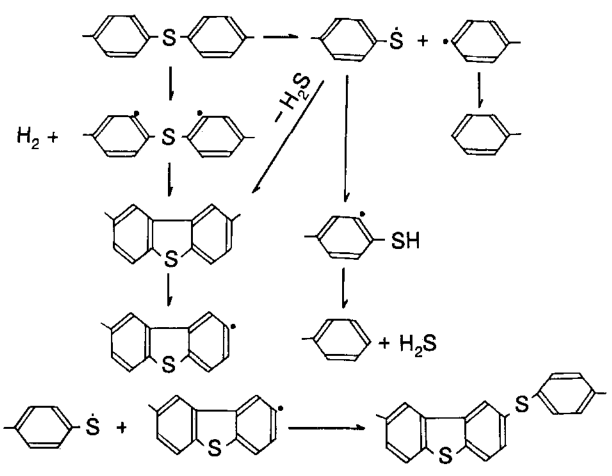

Figure 7 Formation mechanisms of the evolved gases shown in Fig 4.

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