Synthesis and Characterization of Mesophase Spheres from Hydropyrene

Isao Mochida, Hitomi Hatano*, Yozo Korai and Hiroshi Fujitsu

Research Institute of Industrial Science,
Kyushu University 86, Kasuga 816, Fukuoka, Japan
*Chemical Research Center, Kawasaki Steel Corp.,
Kawasaki-cho, Chiba 260, Japan

Carbonaceous mesophase spheres were prepared from a hydropyrene pitch selectively through two stages, the first and second steps of which were heat-treatment at 430 °C under vacuum and at 400 °C under rapid nitrogen flow, respectively. Spheres were isolated by pyridine extraction to define their structure as well as the chemical components by means of optical micrograph, scanning electron micrograph, solvent fractionation and gel permeation chromatography. The spheres of Brooks - Taylor stacking arrangement were found to be mainly composed of condensed trimer, tetramer and pentamer of pyrene units.

Introduction

Carbonaceous mesophase spheres have been well recognized to play an important role during the carbonization as an intermediate for the needle coke and high performance carbon fiber precursor. Recently, the isolated spheres have been proposed to be excellent raw materials for isotropic carbon of high mechanical strength and for spherical column packing of the liquid chromatopraphy. However, their yield was rather low because they tend to form the bulk shape through the growth, coalescence and sedimentation as well documented when the heat-treatment time is prolonged to increase their yield.

The present authors reported that spheres of uniform size could be prepared selectively from hydropyrene through their precipitation in the isotropic pitch which was prepared by the refluxing heat-treatment and succesive devolatilization with rapid nitrogen flow(1).

In this report, present authors are going to describe a better procedure for the selective preparation of mesophase spheres from hydropyrene through two stage heat-teatment under evacuation and under atmospheric nitrogen flow. The structure and chemical components of the spheres thus prepared are also described.

Experimental

Pyrene which was partially hydrogenated by Liethylenediamine was treated at 150 °C for 24 hr in nitrogen flow in a pyrex tube with a reflux condensor under stirring (hydropyrene pitch; HPP) and then air-blown at 250 °C for 6 hr (oxidized hydropyrene pitch: OHPP). The resultant pitch was evacuated (1 mmHg or 0.3 mmHg) at 430 °C for 10 30 min, and were further soaked at 400 °C for 2 hr in atomospheric nitrogen flow to prepare the mesophase pitch. The mesophase pitch was cooled by the rate of 1 °C/min to room temperature to precipitate the spheres.

Mesophase spheres in the mesophase pitch were isolated by pyridine extraction.

Results and Discussion

Preparative conditions of mesophase pitches containing spheres and their optical textures are shown in Table 1 and Fig.1, respectively.

The yield of the pitches varied from 17 % to 43 %. The two stage heat-treatment (Runs 4 and 5) gave larger yield and spheres of more uniform size than those by a single stage under evacuation.

By comparing Runs 4 and 5 where the pressures of 1st stage were variable, the lower pressure decreased the yield as well as size of spheres but increased thier number significantly.

Fig. 2 shows the scanning electron micrographs of spheres isolated as the pyridine insoluble fraction of the pitches produced by Runs 4 and 5. Spheres sticked together because of remaining matrix although their spherical shapes were clearly distinguishable. Some spheres in Fig.4-a were deformed to show flat surfaces, suggesting that they were soft enough to be easily deformed by the glass wall of the flask.

The solubilities of some mesophase pitches are summarized in Table 2. The evacuating or nitrogen blowing heattreatment increased and concentrated the BI fraction to around 90 %. As the PI fraction appears to correspond to the mesophase spheres,

Table 1 Preparative conditions and yields of mesophase pitches

Run No.		HTT (°C/min)	press. (mmHg)	cooling rate (°C/min)	residual*) pitch yields (wt%)
1		430- 10	1.0	1.0 **)	22
2		430- 30	1.0	R.Q	17
3		430- 20	0.3	1.0 **)	19
4	1st	430- 10	0.3	R.Q	32
	2nd	400-120	A.P	1.0	31
5	1st	430- 10	1.0	R.Q	-
	2nd	400-120	A.P	1.0	43

*) original hydropyrene base,
**) to 400°C R.Q; rapid quenching, A.P.; atmospheric pressure

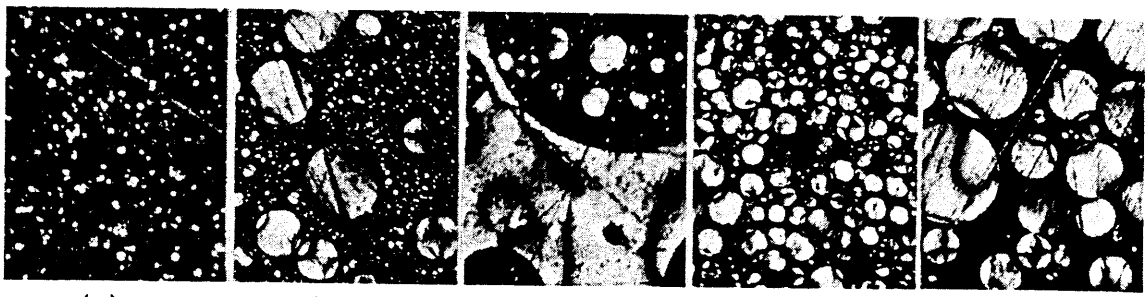

Fig.1 Optical micrographs of mesophase pitches
(a) Run 1 , (b) Run 2 , (c) Run 3 , (d) Run 4 , (e) Run 5

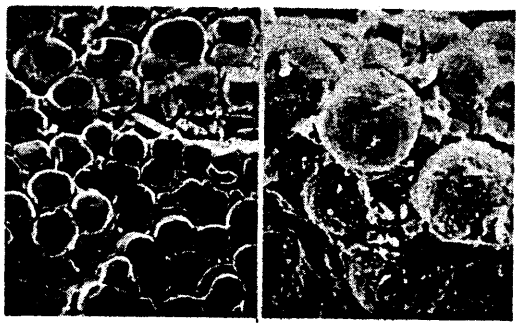

Fig.2 Scanning electron micrographs of spheres isolated by pyridine extraction
(a) Run 4, (b) Run 5

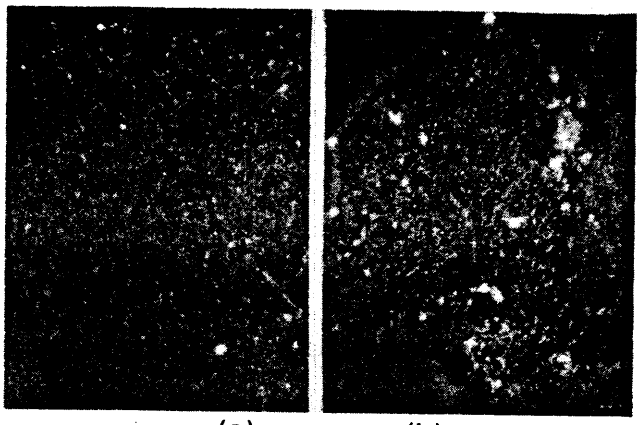

Fig.3 Optical micrographs of BS and BI-PS fractions
(a) BS , (b) BI-PS

their yield were calculated, taking account of mesophase pitch yield (Table 1). The highest yields were as high as 60 % (mesophase pitch base) and 22 % (starting HP base). The two stage treatment of Run 4 is very effective to remove the BS fraction as shown in Table 2.

The micrographs of Fig. 3 show that both BS and BI-PS fractions in the mesophase pitch were isotropic.

The gel permeation chromatograms of the fractions in mesophase pitch are illustrated in Fig. 4. All fractions consisted of dimer, trimer, tetramer and pentamer of pyrene unit, no significant difference except for no dimer in PI-QS being observed.

The microanalyses of the fractions in mesophase pitches indicated that BS, BI-PS and PI fractions had C/H atomic ratios of 1.7, 1.9 and 2.2 respectively, regardless of the mesophase pitch. Thus, the solubility of the mesophase pitch appears to depend on the extents of dehydrogenation and oligomerization, the first factor being dominant.

Table 2
Solubilities of mesophase pitches

Run No.		BS	BI-PS	PI
		(wt%)		
Run 2		12	40	48 (8)
Run 4	1st	10	39	51 (-)
	2nd	4	35	61 (19)
Run 5		13	36	51 (22)

( ) ; original hydropyrene base

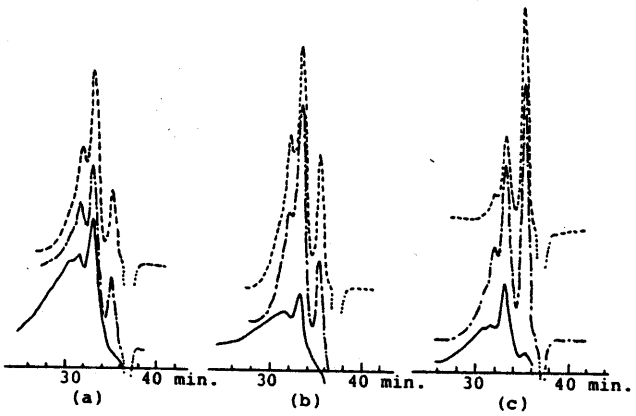

Fig. 4 G.P.C of fractions of mesophase pitches
(a) Run 4-1st, (b) Run 4-2nd, (c) Run 5
-----BS, —·—·— BI-PS, ——— PI-QS

Based on these results, the mechanism for selective precipitation of the anisotropic spheres from mesophase pitch can be discussed. The large aromatic molecules of QI (larger than pentamer) may construct stacking skelton the anisotropic spheres which precipitated from the isotropic matrix on cooling occuluding less-soluble trimers, tetramers and pentamers because of extensive dehydrogenation.

(1) I.Mochida, K.Tamaru, Y.Korai, H.Hatano
Carbon in press.