Thermotropic Behaviors of the Mesophase Pitch Derived from Coal Tar Pitches

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Thermotropic behaviors of a mesophase pitch derived from coal tar pitches were observed under a hot stage microscope to reveal their liquid crystal natures. The behaviors of the mesophase pitch thus observed are discussed schematically.

Introduction

The thermal behaviors of the mesophase pitch are most relevant in the carbon technology.(1)

In the present paper, the behaviors of a mesophase pitch prepared from a hydrogenated coal tar pitch were observed under a hot-stage microscope during the repeated heating and cooling. Although some coal tar pitches have been reported to be difficult for the hot-stage microscopy, the hydrogenation of the pitch allowed easy observation of its mesophase behaviors.

Experimental

Quinoline insoluble (QI) free coal tar pitch obtained by anti-solvent method, was hydrogenated with a Ni-Mo catalyst and then distillated to raise softening point. Analytical data of this pitch were listed in Table 1. The pitch was heattreated in a Pyrex flask for 10 hr at 400°C under rapid nitrogen flow. Thickness of the pitch on the wall of the flask was limted under 3 mm to assure the smooth mass transfer. Thermal behaviors of the mesophase pitch thus prepared were observed on an hot-stage (Leitz 1350) under a polarized-light microscope.

Results

Table 1 summarizes a series of observations on the behaviors of mesophase pitch. The appearances of the mesophase pitch under the respective conditions are shown by the photograph 1 to 10. The mesophase containing pitch, exhibited anisotropic spheres (30vol%) at room temperature. The major anisotropy disappeared by heating up to 400°C, leaving several small anisotropic spheres. Further temperature rising to 420°C at the heating rate of 3°C/sec removed all spheres to give complete isotropy to the pitch. By holding the pitch for 20min at this temperature, anisotropic spheres reappeared and grew in their diameter. The cooling to 390°C and 360°C allowed further growth of spheres, and development of many small spheres and isotropic spots (2) within the large spheres, respectively.

By the second heating to 410°C, small spheres disappeared and isotropic spots coalscence. At 450°C isotropic spots disappeared and appearance, growth, and coalscence of spheres were observable for following 20min. More anisotropic area was observed in the pitch than that at 420°C of the first heating.

Table 1. Sample Properties

Carbon, wt%	91.3
Hydrogen, wt%	6.1
Nitrogen, wt%	0.94
Sulfur, wt%	0.23
H/C, mol ratio	0.80
Toluene, insoluble, wt%	2.2
Carbon residue, wt%	25.8
Softening point, °C	56.5
Aromaticity, ^{13}C NMR	0.78

On cooling, the pitch repeated similar behaviors observed on the first cooling although anisotropic content was larger.

The each states of the pitch observed under a hot stage microscope were examined after rapid quenching. The heating rate was enough rapid (3°C/sec), the surface of the sample exhibited the same feature to that observed under the hot stage microscope.

The isotropic spots were also observable on the vertical sections to distribute from top to bottom, suggesting their sizes according to their location. The spheres were found to distribute near the free surface and on the wall of the vessel by the slow cooling (1°C/min).

Discussion

A mesophase containing pitch derived from a hydrogenated coal tar pitch exhibited a variety of appearances in terms of its optical anisotropy. The appearances of a pitch should reflect both its chemical constituents and phases subjective to the extent of cendensation and the surrounding temperature, respectively. When the rapid heating to an elevated temperature can be assumed to provide phase changes with least change of chemical constituents, the series of observation in the present study are located in a diagram illustrated in Fig 1, where the ordinate and abscissa axises show the temperature and average extent of condensation (or severity of carbonization), respectively.

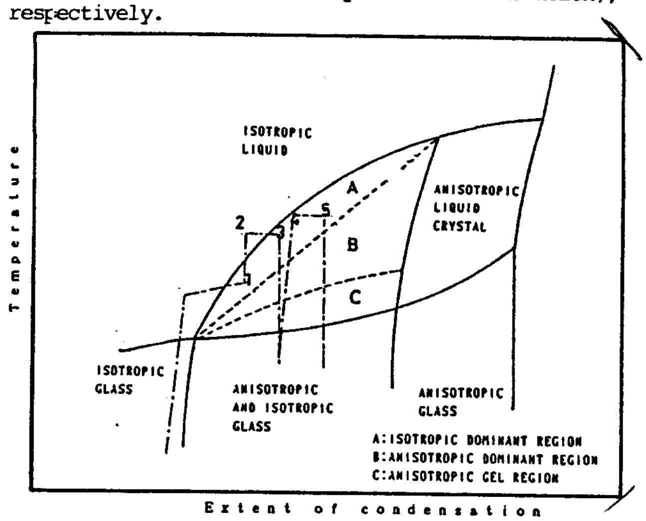

Fig. 1. Phase changes with changes of temperature and condensation

The higher extent of condensation (less smaller constituents) and lower temperature are favorable for the anisotropic development since the ordered stacking of aromatic constituents is stabilized. Thus, the regions of complete isotropy, A (Isotropic dominant) and B (Anisotropic dominant), in Fig. 1 are reasonably defined. The rapid heating and cooling with no change in chemical constituents allowed the reversible changes among these states.

Development of isotropic spots on the cooling (region (C)) may look strange from the above understanding. The smallest constituents which are anchored in the stacking layers of larger constituents to exhibit optical anisotropy may be expelled out to form the isotropic phase because the decreased mutual solubility due to the lower temperature does not allow their stay in the layer.

Table 2. Results of the Hot Stage Observations

No.	Phase	Heat Treatment Conditions	Photo. No.	Hot Stage Observations
---Heating 1°C/sec---				
First Circulation				
1	1	400°C	1	small spherical meso.
2		heating 3°C/sec		
3	2	420°C	2	disappearance of meso.
4		keeping 20 min		meso. appears, grows
5	3	420°C	3	spherical meso.
6		cooling 3°C/sec		
7		390°C	4	growth of spherical meso.
8		360°C	5	appear. of isotropic spots
---Second Circulation---				
9		heating 3°C/sec		
10		410°C	6	exhaust spherical meso.
			7	coalescence of isotropic spots, decrease of sand-like meso.,
11	4	450°C		disappearance of isotropic spots
12	5	keeping 20 min		coalescence and growth of meso.
13		cooling 3°C/sec		
14		420°C	8	appear. of sand-like meso.
15		390°C	9	growth of spherical meso.
16		380°C		appear. of isotropic spots
17		360°C	10	further growth of spherical meso.

References
1. R. J.Diefendorf, 16th Conference on Carbon, Abstracts, p26 (1983)
2. I. Mochida, K. Tamaru and Y. Korai, Carbon, 22, 181 (1984)

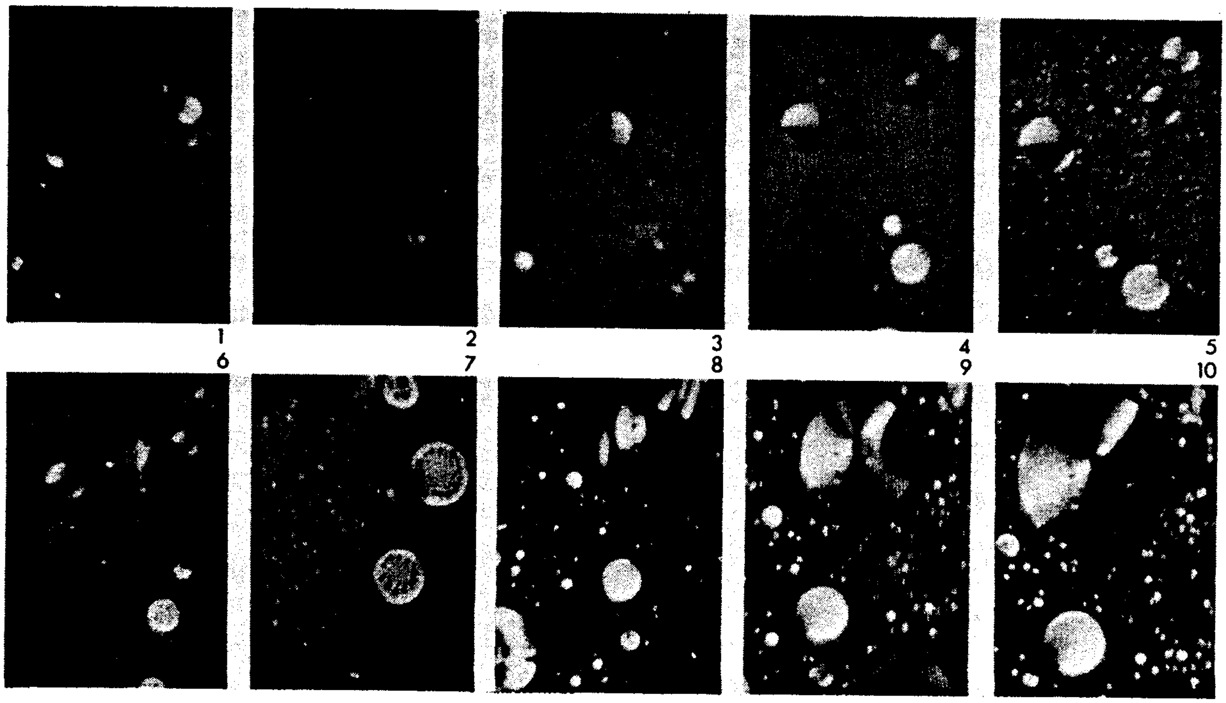

Fig. 2. Ten photographs depicting the appearance of mesophase pitch under conditions described in Table 2.