CARBON XXX (2014) XXX–XXX

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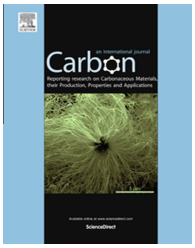

The thermotropic liquid crystalline behavior of mesophase pitches with different chemical structures

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ARTICLE INFO

Article history:
Received 30 May 2014
Accepted 3 October 2014
Available online xxxx

ABSTRACT

Chemical structure-dependent liquid crystalline behaviors of two commercial mesophase pitches, M-AR and T-MP, which are synthesized with different raw materials of naphthalene and coal tar, respectively, were comparatively examined. The NMR analysis together with preparation procedure enabled us to suggest that M-AR consisted of linear semi-rigid molecules and T-MP, irregularly shaped rigid molecules. Between 320 and 370 °C M-AR showed marbled texture whereas T-MP, a change from schlieren/marbled to schlieren texture. WXRD results indicated that M-AR exhibited a gradual change of d_{002} and L_c with temperature but T-MP, a drastic change. A point shear stress made M-AR produce oriented flow domains but T-MP retained schlieren texture even in the oriented structure. In the temperature range producing biphase, M-AR showed a shoulder on the plot of viscosity versus temperature but T-MP, a peak. As temperature was increased M-AR gave an increase of loss tangent but a decrease of yield stress while T-MP gave a saturation point at 330 °C, at which temperature loss tangent was maximum and yield stress was minimum. Both mesophase pitches gave viscosity curves matched with the Asada–Onogi model. In the temperature range producing dispersed polydomain system, however, T-MP showed almost shear rate-independent plateau while shear-dependence was observed in M-AR.

1. Introduction

Synthetic pitches are classified into two categories, isotropic and mesophase. Mesophase pitches are being used in the manufacturing of pitch based high performance carbon fiber. The high carbon yield offers a good balance of cost and effectiveness [1]. In particular, the exceptionally high thermal-conductivity enables mesophase pitch based carbon fiber to be used as a core part of nuclear-submarines or atomic reactors [2]. To design the fabrication process it is prerequisite to understand the liquid crystalline properties of the pitches with respect to temperature and shear rate. Most of the mesophase pitches are composed of molecules whose chemical structure is not clearly defined [3–6]. The wide molecular weight distribution further makes the interpretation of the physical properties of the pitches difficult. In spite of the

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http://dx.doi.org/10.1016/j.carbon.2014.10.007

Please cite this article in press as: Lee S et al. The thermotropic liquid crystalline behavior of mesophase pitches with different chemical structures. Carbon (2014), http://dx.doi.org/10.1016/j.carbon.2014.10.007

successful commercialization of high performance carbon fibers from the mesophase pitches, only limited information on the physical properties of the pitch is available. To make the problems simpler, some carbon researchers have concentrated on the production of mesophase pitches whose chemical composition can be defined [7–13].

It has a practical importance to relate the morphological and rheological properties to the chemical structure of the mesophase pitches [14–18]. Because of the irregularity of the molecules of mesophase pitches, however, controversy as to the results still remain. In this study, the effect of the chemical structure of mesophase pitch molecules on the liquid crystalline behavior was investigated with respect to the shape and rigidity of pitch molecules by choosing two representative commercial mesophase pitches, M-AR of Mitsubishi Gas Chemical Co. and T-MP of Toray. The difference in the chemical structures of pitch molecules was assessed by NMR spectroscopy and preparative methods of the mesophase pitches. Based on the assessed chemical structure, the characteristic liquid crystalline responses and phase change of the two mesophase pitches were discussed in terms of thermal and shear histories.

2. Experimental

2.1. *Materials*

Two commercial grade mesophase pitches by Mitsubishi Gas Chemical Co. (M-AR) and Toray (T-MP) were used. M-AR is reported to be synthesized by catalytic polymerization of naphthalene using HF/BF_3 as a catalyst [19], T-MP, by thermal polycondensation and subsequent distillation of coal tar [20]. M-AR and T-MP showed a softening point at 270 and 275 °C, respectively.

2.2. *Measurement of physical properties*

The chemical structure of the mesophase pitches was identified by solid-state ^{13}C NMR (NMR, JNM-ECA-800, JEOL). The NMR samples were filled in a 3.2 mm NMR cell with sealing caps. ^{13}C single-pulse NMR spectra were obtained at 15 kHz of magic angle spinning (MAS) speed at 25 °C. Thermal properties were measured by differential scanning calorimetry (DSC, SDT Q600, TA instruments) in N_2 atmosphere at the scanning rate of 10 °C/min.

The liquid crystalline texture was observed by polarized optical microscope (POM, BX51, Olympus) equipped with CCD camera (HFX-11A, Nikon) and heating stage (FP-82HT, Mettler Toledo). The molecular ordering in the as-powder and molten state was estimated by Raman spectra (NRS-3100, JASCO) with argon ion of 514.5 nm. The liquid crystalline structure was examined by wide angle X-ray diffractometer (WXRD, Xps GADDS, Bruker) with Nickel filtered CuKα radiation of 40 kV and 45 mA. Scanning experiment was carried out on the equator over the 2θ range of 0–40° at the scan speed of 0.05°/min. The interlayer spacing (d_{002}) of the graphitic crystal of (002) plane and the crystal thickness (L_c) were calculated by Bragg (1) and Scherrer (2) equations, respectively [21,22].

$$n\lambda = 2d\ \sin\theta \tag{1}$$

$$L_c = \frac{K\lambda}{\beta\ \cos\theta} \tag{2}$$

in which, θ is the scattering angle, λ is the wavelength of the X-rays used, and β is the half-maximum line width in radian. The form factor K is 0.9 for L_c according to Jeffrey et al. [23]. The values of d_{002} and L_c of as-power samples were evaluated at 25 °C. Further, the variation of d_{002} and L_c with temperature was identified over the temperature range of 260–440 °C at the heating rate of 20 °C/min.

Rheological properties were measured by Advanced Rheometric Expansion System (ARES, TA Instruments) in N_2 atmosphere. A parallel plate geometry with a diameter of 25 mm was adopted. The plate gap and strain level were 0.8 mm and 5%, respectively. The ARES specimens were stabilized on the plate for 15 min before measurement to fully relax residual stress.

3. Results and discussion

The chemical composition and structure of the commercial grade mesophase pitches, M-AR and T-MP, are not well defined. According to Flory et al. [24,25], however, the chemical nature of the mesophase pitch molecules, particularly shape and rigidity, would have a significant effect on their liquid crystalline behavior. The molecular architecture of M-AR and T-MP was quantitatively identified by ^{13}C NMR spectroscopy [26].

Fig. 1 shows NMR spectra of M-AR and T-MP. According to the method suggested by Diaz et al. [27], the distributions of aromatic and aliphatic carbons and the aromaticity values of the mesophase pitches were calculated and listed in Table 1. T-MP gives much greater value of the aromaticity than M-AR, which indicates that T-MP has a more rigid structure than M-AR. Given the aromaticity values, T-MP is supposed to largely consist of rigid aromatic mesogenic units, whereas M-AR has a semi-rigid structure, in which the mesogenic units are connected by non-aromatic components such as aryl-aryl bonds, naphthenic rings, or alkyl groups [12,19]. The result is in line with the preparation methods of the mesophase pitches [28]. T-MP is prepared by polycondensation and subsequent distillation of coal tar in which almost all of the thermally unstable aliphatic groups are eliminated. On the other hand, M-AR is synthesized by catalytic polymerization of naphthalene, in which the non-aromatic C-C bonds exist as connecting groups of rigid mesogenic units. These enable us to depict the schematic molecular structure of T-MP and M-AR as shown in Fig. 2. In other words, T-MP would have a nonlinear and irregular structure but M-AR would have a linear and regular structure, which agrees with previous reports by others [6,12,19,29].

The degree of perfectness of molecular arrangement of M-AR and T-MP in the solid state was evaluated by Raman spectroscopy. Table 2 gives the intensity ratios of D-band to G-band (I_D/I_G) of the pitches in as-powder form. The lower value of I_D/I_G represents the more highly organized phase [30]. M-AR gives lower value of I_D/I_G than T-MP, suggesting more highly arranged state. The molecular ordering of the mesophase pitches is more clearly assessed by the distance

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