

PREPARATION OF MESOPHASE PITCH FROM METHYLENE-BRIDGED AROMATIC OLIGOMERS

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Introduction

Mesophase pitch, which has been recognized as an excellent precursor for advanced carbon materials, is required to have better properties. These properties have a delicate dependence on the chemical structure of the constituent molecules. When a complicated mixture such as a petroleum residue or a coal tar pitch is used as a raw material, it is difficult to control the chemical structure and the molecular weight distribution of derived pitch. To solve these problems, some researchers^[1,2] have developed several procedures to synthesize mesophase pitch from aromatic hydrocarbons.

Yanagida et al.^[2,3] reported two-step preparation of mesophase pitch from C₈~C₁₀ alkylbenzene, where alkylbenzene is first coupled by CH₂ linkage and then heat treated into mesophase pitch. However, alkylbenzene is a mixture, containing methyl, ethyl, propyl and butyl on various sites of benzene ring, and it is relatively hard to control the carbonization reactivity and structure of product. In this paper, two kinds of pure model aromatic compounds, i.e. 1,2,4,5-tetramethylbenzene (Durene, Du) and tetrahydronaphthalene (Tetralin, Te) were chosen as the feedstocks, in order to reveal the details of the formation and structural features of mesophase pitch and obtain spinnable mesophase pitch through methylene bridge cross-linkage and successive heat treatment.


Experimental

Durene or tetralin (purity >97%), sym-trioxane (purity >97%, as cross-linker) and paratoluenesulfonic acid (PTS, analytically pure, as catalyst) were mixed in a certain ratio in a flask and heated to 80-180°C soaking for 6 hours with continuous stirring under N₂ atmosphere. After removing PTS by washing repeatedly with water, the product was extracted with hot alcohol or n-heptane to remove the unreacted durene or tetralin, and then carbonized in a steel tube bomb under N₂ bubbling to get mesophase pitch. The oligomers and TS fractions of mesophase pitches were analyzed by the ¹H-NMR (Varian FT-80A), Low Voltage EI-MS (JMS-D300S) and FDMS (Finnigan-MAT 90).

Results and Discussion

1. Structural features of aromatic oligomers

Fig.1 is the ¹H-NMR spectra of Du- and Te-oligomers. Fig.2 shows the low Voltage EI-MS

spectrum of Du-oligomer. In Fig.1 a resonance between 3 and 5ppm can be found, which is assigned to methylene bridge hydrogen, suggesting the model aromatics were conjugated with methylene to form polymers. For Du-oligomer (Fig.1-a), the peaks at 2.1ppm and 1.9ppm are the different positional methyl hydrogen absorptions (1.9ppm ascribed to steric hindered methyl hydrogen, ). The hydrogen atomic ratio of aromatic, methylene and methyl 2:3.35:25.35 reflects that the principal component of this oligomer is dimer and trimer, that is also proved by the result of EI-MS analysis in Fig.2 (m/z 280, dimer; 426, trimer; 572, tetramer; and so on). According to Fig.1-b, Te-oligomer is mainly composed of trimer to tetramer, the resonance at 2.5ppm and 1.68ppm ascribed to H_α and H_β hydrogen of naphthenic group, respectively.

2. Properties and component structures of mesophase pitches

Spinning mesophase pitches with 100vol.% flow domain optical texture derived from Du- and Te-oligomers were prepared by heat treatment. The preparation conditions and some properties of mesophase pitch are summarized in Table 1. Du-oligomer can form full flow type mesophase at relatively low temperature (360°C), reflecting the very different chemical nature of this oligomer in comparison with conventional pitch such as a petroleum residue or a coal tar pitch. The mesophase pitch has not only high anisotropic content, but also low softening point, high solubility, high H/C and good flow characteristic in the temperature range of 295°C to 330°C. Fig.3 shows the FDMS pattern of TS fraction of mesophase pitch from Du-oligomer (Du-360-17-TS). Peaks were divided into the groups of tetramer series (MW:400-550), pentamer series (MW:550-650), hexamer series (MW:650-760) etc. In each group, molecular weight changes by 14 with the number of methyl groups and by 2 with the number of naphthenic rings. According to the results of FDMS and ¹H-NMR (Fig.4), the possible structure models of Du-360-17-TS can be illustrated in Fig.5. The structural characteristics of mesophase pitch from Du-oligomer are summarized as follows: a. cata-type aromatic skeleton. b. a lot of methyl groups and some amount of naphthenic and methylene groups. c. very similar structures. In comparison with Du-oligomer, the Te-oligomer

forms mesophase at a rather high temperature(415°C), resulting from the complicated components of carbonization product. FDMS analysis of the TS fraction of mesophase pitch (Te-415-10-TS) indicated that, besides the decomposition, the thermal recombination, hydrogen transfer reaction and cyclization also occurred in the carbonization system. Fig.6 shows the possible reaction schemes for Te-415-10 from ¹H-NMR and FDMS.

Reference

- 1.I. Mochida et al Carbon 27, 311 (1989)
- 2.A.Sakanishi et al Carbon 30, 459 (1992)
- 3.K.Yanagida et al 20th Bienn. Conf. on Carbon, Extended Abstracts, 160 (1991)

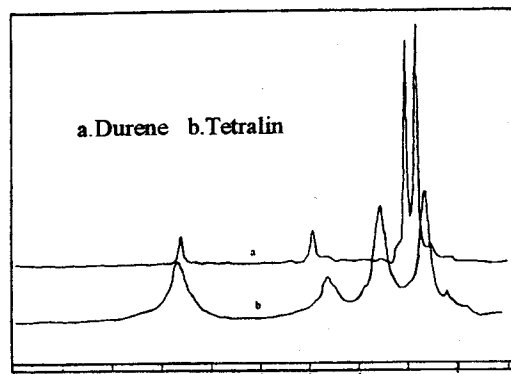


Fig 1. ¹H-NMR spectra of oligomers

Table1. Preparation conditions and some properties of mesophase pitches

Assignment	Heat treatment conditions Temperature-time °C-h	Anisotropic content Vol.%	Softening point (°C)	H/C	Solubility		
					TS	TI-PS	PI
Du	360-17	100	260	0.86	30.0	18.5	51.5
Te	415-10	100	290	0.58	44.4	14.4	41.2

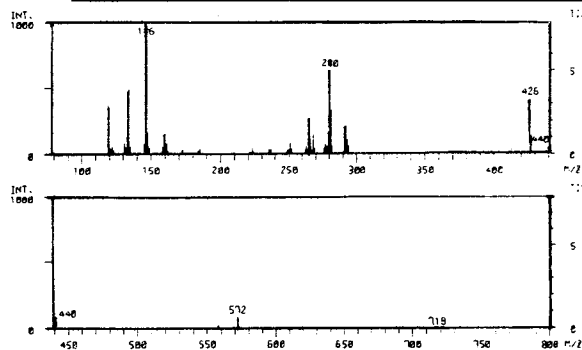


Fig.2. Low Voltage EI-MS spectrum of Du-oligomer

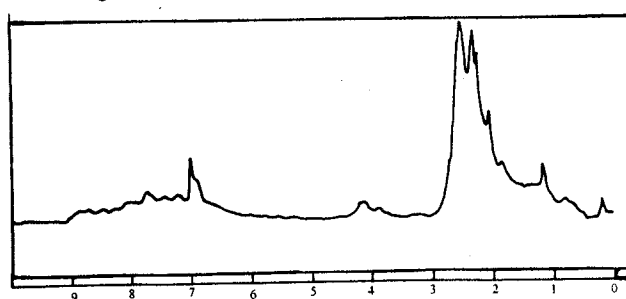


Fig.4. ¹H-NMR spectrum of TS fraction of mesophase pitch derived from Durene

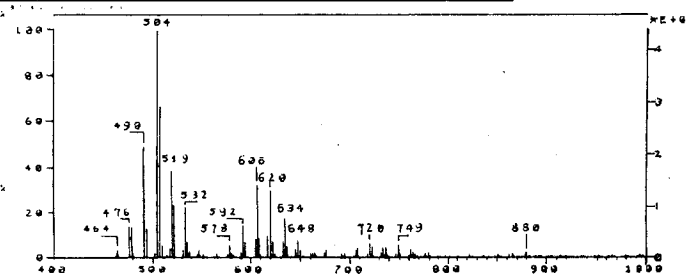


Fig.3. FDMS pattern of TS fraction of mesophase pitch derived from Durene

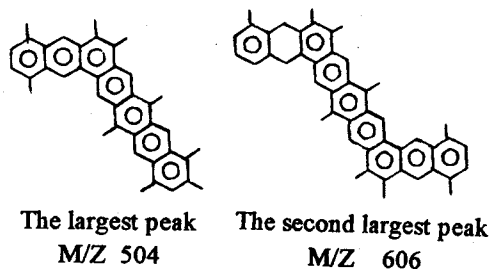


Fig.5. Possible models of Durene-360-17-TS

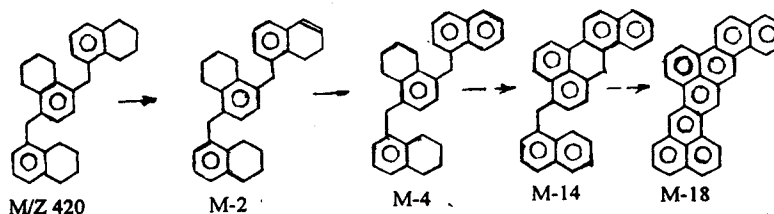


Fig.6. Possible reaction scheme for carbonization of Te-oligomer