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1. Introduction

Mesophase pitch is widely recognized as an excellent precursor for making high quality carbon materials.¹ Mesophase pitch based carbon material has great exploitation potential and broad application prospects in the field of new carbon materials due to its relatively low price, high strength, good electric performance, and environmental friendliness *etc.*^{1–4} Naphthenic base oil which contains a high content of aromatic fractions can be used for the preparation of high-quality mesophase pitch; moreover, the naphthenic vacuum residue is abundant in source and cheap in price.^{5,6} Therefore, research on the preparation and formation mechanism of petroleum based mesophase pitch are a hotspot and focus in the field of carbon materials at home and abroad.^{7–9}

As previously reported, the number of alkyl groups in the raw material was one of the most important factors to control the solubility and the anisotropic content of mesophase pitch.^{8–11} The effect of the alkyl groups on the formation of mesophase pitch has been studied. Some research has indicated that the

alkylation method was quite an effective method to improve the properties of mesophase pitch.^{11–15} Miyake *et al.* have tried to assess the effects of alkyl groups on the formation of anisotropic texture.¹⁵ In their work, a mesophase pitch, which contained only a few alkyl groups per molecule, was treated by reductive alkylation (methyl and ethyl) to study the effects of reductive alkyl groups on anisotropic texture formation. When the alkylated pitch was carbonized, the anisotropic content varied depending on the number and steric size of introduced alkyl groups. After studying the preparation of naphthalane and methyl naphthalane mesophase pitches, Mochida *et al.* found that hydromodification of the feedstock is effective method to convert quinoline insolubles of pitches into graphitizable carbon.^{16–18} Furthermore, Korai *et al.* suggested that the content of methyl in the mesophase molecule is the main influence factor of mesogen molecules stacking.¹⁹ Yoon *et al.* also proposed that the number of methyl groups have an influence on the properties of the mesophase pitch. In conclusion, the influences of the alkyl side chain and naphthenic group on the optical texture and molecular structure of mesophase pitch are worth to be studied comprehensively.²⁰

In this paper, the naphthenic-based aromatic-rich fraction were subjected to the hydroalkylation treatment by reacting with tetrahydronaphthalene and polyethylene glycol, and then the modified materials were treated by direct condensation method to study the influences of hydromodification of feedstocks on the development of mesophase structure. In addition,

^aCollege of Chemical Engineering, Qingdao University of Science and Technology, Qingdao, China, 266042. E-mail: yushitaoqu@126.com; djw1970@163.com; Fax: +86 0532 84022782; Tel: +86 0532 84022782

^bState Key Laboratory of Heavy Oil Processing, China University of Petroleum, Qingdao, China, 266580. E-mail: ldongupc@vip.sina.com; Fax: +86 0532 86984629; Tel: +86 0532 86984629



the influences of the naphthenic structures and alkyl chains in modified materials on the formation of mesophase pitches were investigated, and the mechanism of carbonization was discussed.

2. Experimental section

2.1 Materials

The aromatic-rich fraction (named F) was derived from the naphthene-based vacuum residue provided by CNOOC Company. The additives tetrahydronaphthalene and polyethylene glycol are supplied by Aladdin Industrial Corporation, and the average molecular weight (M_n) of polyethylene glycol is about 400. Table 1 listed the properties of the feedstock. The F was characterized with high content of carbon and low contents of sulphur and nitrogen. Additionally, the aromatics were enriched in F, while no asphaltene was detected.

2.2 Hydromodification and thermal treatment

The feedstock F together with additives (tetrahydronaphthalene or polyethylene glycol) were heated in the 300 ml high-pressure agitated autoclave after replacing air the reaction system by nitrogen for 3 times. When the hydroalkylation reaction was carried out under autogenic pressure at 400 °C for 2 hours, the unreacted additives were purged from the reaction system by nitrogen and the modified materials were generated at the bottom of autoclave. Then the modified materials were heated in to 430 °C with a rate of less than 5 °C min⁻¹. The reaction was conducted under the pressure of 2 MPa for 9 hours and the mesophase pitch were obtained.

2.3 Analysis

The simulated distillation technology was used to determine the IBP (initial boiling point) and FBP (final boiling point) of modified material on a CP3800 gas chromatograph made by America Varian Company according to ASTM D-2887. The elemental composition of modified material was determined by a PE-2400 Series HCSN elemental analyzer. The functional groups in aromatic compounds were characterized by FTIR analysis using a Nicolet S-215 spectrometer. The optical texture of mesophase pitch was observed and photographed on a XP-4030 polarized microscope made by Shanghai Milite Precise Instrument Co. Ltd, China. The penetrometer method was used to measure the softening point (SP) of mesophase pitch.²¹ The carbon residue of the carbonized product was analyzed in accordance with ASTM D4530. The modified materials and the pyridine-soluble fractions of mesophase pitches were characterized by ¹H NMR on a Bruker Avance DMX-500 NMR

spectrometer using deuterated pyridine as the solvent. The crystal structure of the mesophase pitch was characterized by a PANalytical X'Pert PRO MPD X-ray diffraction (XRD) with a Cu K α radiation ($\lambda = 0.15418$ nm). The Raman spectra of products were obtained in a Labram 10 Raman spectrometer (Jobin Yvon Company) using a He-Ne laser as excitation source giving a monochromatic red light ($\lambda = 632.8$ nm) at 1 mW.

3. Results and discussion

3.1 Characterization of modified materials

3.1.1 SIMDIS and elemental analysis. The SIMDIS analysis was used to certify whether the modified materials contain modifying agents (tetrahydronaphthalene or polyethylene

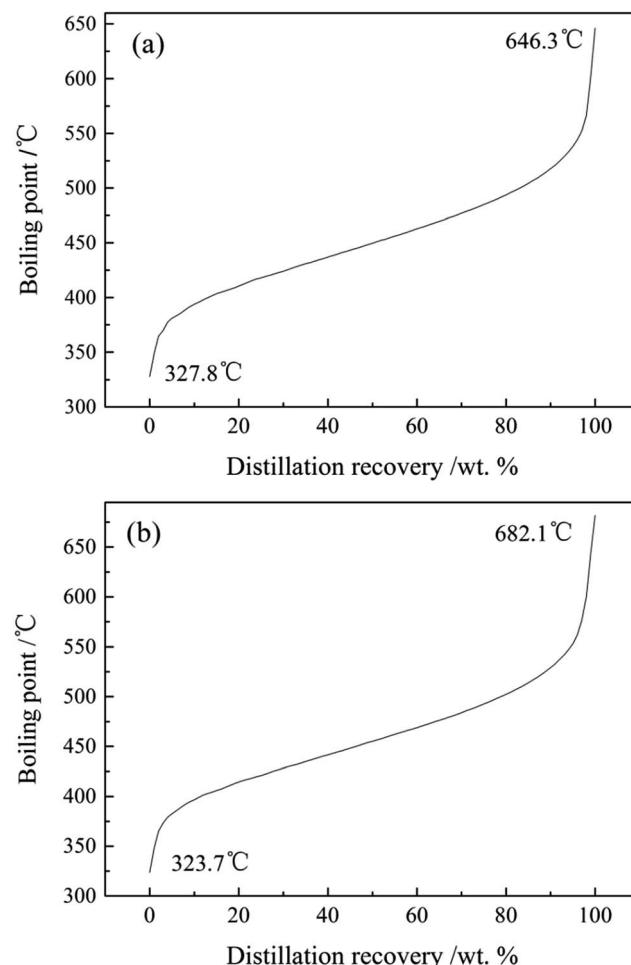


Fig. 1 SIMDIS characteristic curves of modified materials: (a) T4; (b) E4.

Table 1 Elemental composition, relative molecular mass and four components of F

Sample	Elemental composition/wt%					Group composition/wt%			
	C	H	N	S	M_n	Saturates	Aromatics	Resin	Asphaltene
F	90.22	9.64	0.09	0.04	410.12	14.47	56.40	30.15	0



Table 2 Elemental components of modified materials^a

Sample	Elemental component/wt%			$n(\text{H})/n(\text{C})$
	H	C	O	
F	8.37	89.84	0.001	1.1180
T1	8.45	89.96	0.001	1.1272
T2	8.72	89.90	0.001	1.1640
T3	8.80	89.86	0.001	1.1752
T4	8.93	89.85	0.001	1.1927
E1	8.46	90.12	0.002	1.1265
E2	8.59	90.03	0.002	1.1450
E3	8.71	89.98	0.002	1.1616
E4	8.35	90.87	0.002	1.1027

^a Note: $n(\text{H})/n(\text{C})$, molar ratio of hydrogen atom to carbon atom.

glycol) after the modification reaction. The feedstock F modified with 5, 10, 20 and 30 wt% of tetrahydronaphthalene were named as T1, T2, T3 and T4, respectively. Similarly, E1, E2, E3 and E4 referred to the modified materials obtained from the modification of F with 5, 10, 20 and 30 wt% of polyethylene glycol. Besides, the feedstock treated without modifying agents under the same modified conditions was labeled as F.

As shown in the SIMDIS characteristic curves of T4 and E4 (Fig. 1), the IBP (327.8 °C) of T4 was higher than the boiling point (207.2 °C) of its modifying agent (tetrahydronaphthalene), and the IBP (323.7 °C) of E4 was below the boiling point (280 °C) of polyethylene glycol. This meant that there were no modifying agents left in the modified materials after the hydro-modification of feedstocks.⁸

Table 2 listed the elemental components of modified materials. Owing to the hydromodification of feedstock, the $n(\text{H})/n(\text{C})$ ratios of modified materials (T1, T2, T3, T4, E1, E2, E3 and E4) were all higher than F. In addition, the oxygen mass percents of modified materials were all below 0.02%, which demonstrated that there was little oxygenic functional group contained in the modified materials.⁸ Therefore, it was ignored that the influence of oxygen during the following thermal reaction.

3.1.2 FTIR analysis. The FTIR spectra of modified materials F, T1, T2, T3, T4, E1, E2, E3 and E4 are shown in Fig. 2. The characteristic bands of polycyclic aromatic hydrocarbons in the region of 730–980 cm⁻¹, as well as the absorption bands of $-\text{CH}_3$ and $-\text{CH}_2-$ (near 1330, 1460, 2850, and 2930 cm⁻¹) were presented in Fig. 2, which implied that the modified materials were polycyclic aromatic compounds with some alkanes.²³ The aromaticity (f_a) of modified materials were defined as $f_a = 0.574\text{Abs}_{1600}/(\text{Abs}_{1600} + 0.16\text{Abs}_{1460} + 0.23\text{Abs}_{1330}) + 0.024$, and the molar ratios of $-\text{CH}_2-$ to $-\text{CH}_3$ (r) were calculated according to the formula $r = 3.07\text{Abs}_{1460}/\text{Abs}_{1330} - 3.72$.²² The marks Abs_{1330} , Abs_{1460} and Abs_{1600} represented the absorption peak areas at 1330, 1460 and 1600 cm⁻¹, respectively. The two parameters (f_a and r) are summarized in Table 3.

As the amount of tetrahydronaphthalene increased, the aromaticity (f_a) of F, T1, T2, T3 and T4 decreased successively. Analogously, the f_a of F, E1, E2, E3 and E4 decreased with the adding of polyethylene glycol (presented in Table 3). This

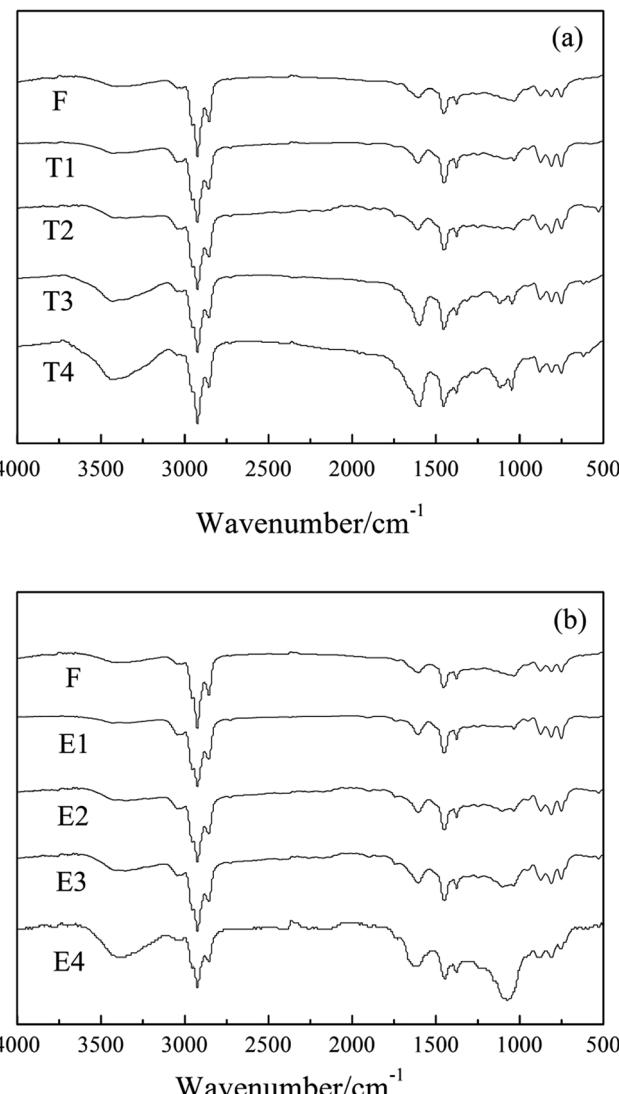


Fig. 2 FTIR spectra of modified materials: (a) F, T1, T2, T3 and T4; (b) F, E1, E2, E3 and E4.

implied that the alkyl structures (include naphthenic structures and alkyl chains) contained in modified materials increased with raising amount of modifying agents.⁸ In addition, the molar ratios (r) of $-\text{CH}_2-$ to $-\text{CH}_3$ of F, T1, T2, T3 and T4 increased in sequence, and those of F, E1, E2, E3 and E4 increased in a similar way. It meant the increase of naphthenic structures or alkyl chains contained in modified materials with the increase of modifying agents.

3.1.3 ¹H NMR analysis. In order to explore the form of alkyl structures existed in the modified materials, the modified

Table 3 Aromatic degrees (f_a) and molar ratios of $-\text{CH}_2-$ to $-\text{CH}_3$ (r) of modified materials

Sample	F	T1	T2	T3	T4	E1	E2	E3	E4
f_a	0.36	0.33	0.31	0.30	0.29	0.34	0.33	0.31	0.30
r	1.75	1.96	2.01	2.11	2.14	1.89	1.92	1.99	2.02

materials (F, T4 and E4) were selected to be analyzed by ^1H nuclear magnetic resonance. The ^1H NMR spectra of the modified materials (F, T4 and E4) are shown in Fig. 3. The

hydrogen distributions and the structural parameters calculated according to the improved Brown–Ladner method²² are summarized in Table 4.

Compared with F, the percent of H_{ar} hydrogens in T4 and E4 decreased, which implied that the aliphatic hydrocarbons increased. The percent of H_{β} in T4 decreased sharply, while that in E4 increased obviously compared with F, meanwhile, the percent of H_{γ} changed little. It suggested that the modified material T4 contained less alkyl chains than F, while E4 possessed more than F.¹⁰ In addition, the percent of H_{n} in T4 and E4 were higher than that of F, and T4 contained more H_{n} than E4 obviously, which meant that the increase of naphthenic structures in T4 and E4 due to the treatment of tetrahydronaphthalene and polyethylene glycol, and T4 contained more naphthenic structures than E4.⁸ This was consistent with the computed results of the naphthenic rings (R_{N}). As shown in Table 4, the naphthenic rings of E4 was much more than F and E4, while the R_{N} of E4 changed little compared to F. It indicated that there were more naphthenic structures in T4 than E4.^{11,22} In consideration of the result of the FTIR analysis, the increased methylene structures in T4 were mainly existed in the form of naphthenic structures, while those in E4 were largely alkyl chains. In conclusion, the increased alkyl structures in modified materials resulted from the modification of tetrahydronaphthalene were mainly naphthenic structures, while those in modified materials treated by polyethylene glycol were largely alkyl chains considering the analyses of FTIR and ^1H NMR.

3.2 Optical texture analysis of mesophase pitch

The optical textures of mesophase pitches prepared by F, T1, T2, T3, T4, E1, E2, E3 and E4 (named F-MP, T1-MP, T2-MP, T3-MP, T4-MP, E1-MP, E2-MP, E3-MP and E4-MP, respectively) are presented in Fig. 4.

As shown in Fig. 4(1), the medium domain structure with a diameter in the range of 100–200 μm was generated in the optical micrograph of F-MP.²⁷ The size of anisotropic unit developed with the adding of tetrahydronaphthalene. When the additive amount was 30 wt%, the large domain structure with a size larger than 200 μm was appeared in T4-MP. This behavior could be explained by the increase of naphthenic structures in modified materials. Hydrogen transfer reactions of naphthenic

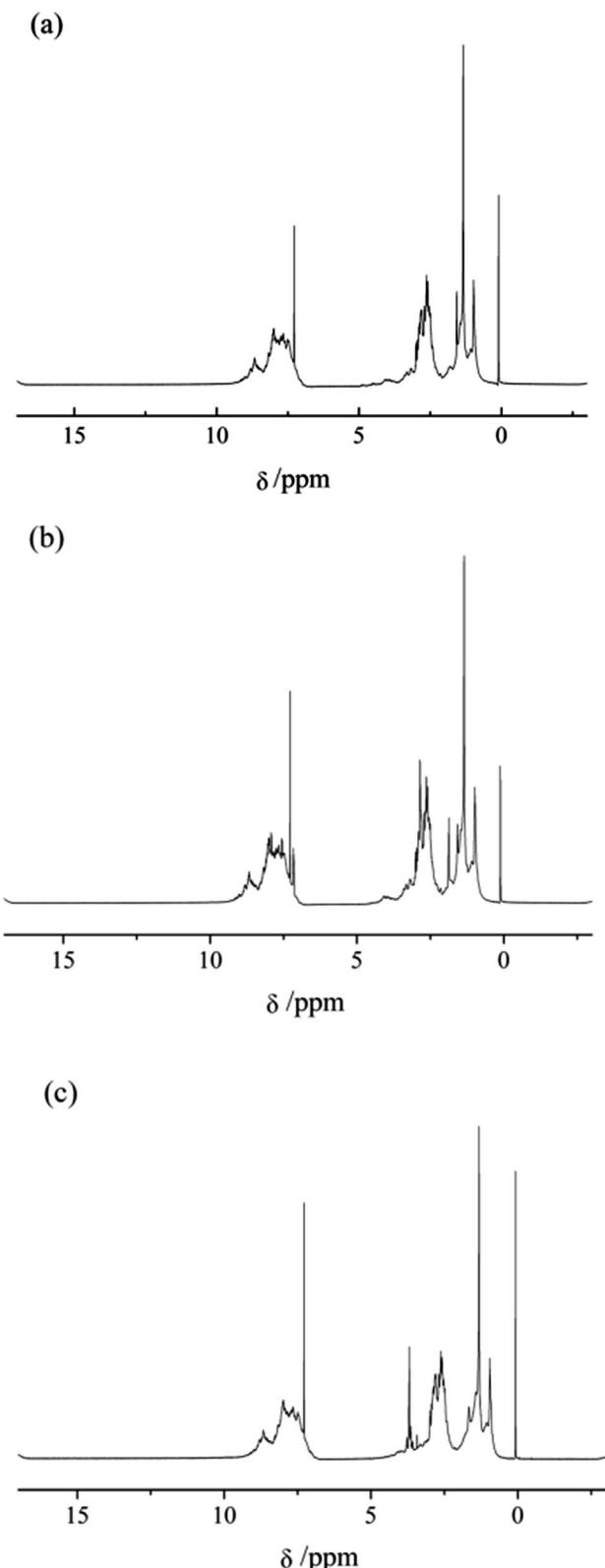


Fig. 3 ^1H NMR spectra of the modified materials: (a) F; (b) T4; (c) E4.

Table 4 Hydrogen distributions of F, T3 and E4^a

Sample	Hydrogen contents/%					
	H_{ar}	H_{α}	H_{β}	H_{γ}	H_{n}	R_{N}
F	42.87	30.31	11.97	4.54	10.31	0.84
T4	34.66	30.55	5.24	5.38	24.17	2.45
E4	32.90	29.95	18.33	7.59	11.23	0.91

^a Note: H_{ar} , aromatic hydrogens ($\delta = 9.0\text{--}6.0$ ppm); H_{α} , aliphatic hydrogens in methyl or methylene groups in α -position to an aromatic ring ($\delta = 3.3\text{--}2.0$ ppm); H_{β} , aliphatic hydrogens in methyl or methylene groups in β -position to an aromatic ring ($\delta = 1.4\text{--}1.0$ ppm); H_{γ} , aliphatic hydrogens in methyl or methylene groups in γ -position to an aromatic ring ($\delta = 1.0\text{--}0.5$ ppm); H_{n} , naphthenic hydrogen ($\delta = 2.0\text{--}1.4$ ppm); R_{N} , the number of naphthenic rings.⁸

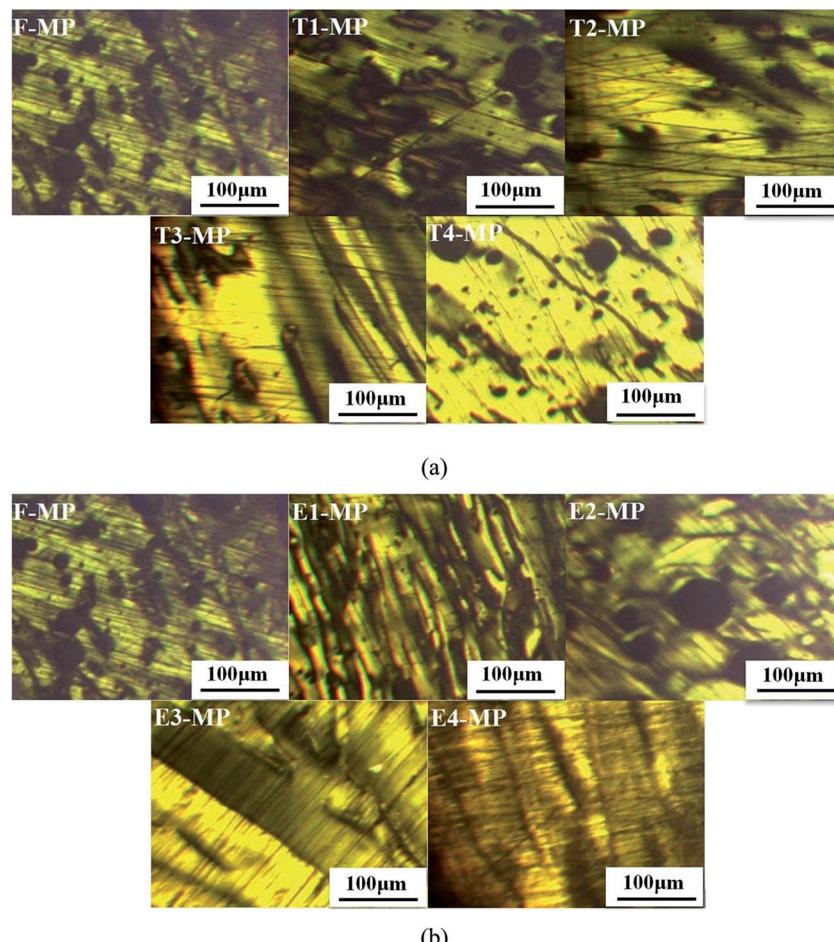


Fig. 4 Optical textures of mesophase pitches: (a) F-MP, T1-MP, T2-MP, T3-MP and T4-MP; (b) F-MP, E1-MP, E2-MP, E3-MP and E4-MP.

structures occurred during the pyrolysis process, which could moderate the violence of the reaction, maintain the flowability of the reaction system, and improve the solubility of mesophase pitch.⁸ Then the development of mesophase pitch undergoes a relative smooth process, and a mesophase pitch with large domain structure was easily formed.

From Fig. 4(2), the optical texture of mesophase pitches (E1-MP, E2-MP, and E3-MP) developed and the diameter of anisotropic units grew larger with the increase of polyethylene glycol. However, when the amount of polyethylene glycol rose to 30 wt%, the mosaic structure with a size smaller than 50 µm was appeared in E4-MP. This phenomenon was ascribed to the overabundance of alkyl chains which would produce more free radicals at high temperature. The free radicals could accelerate the carbonizing rate, so the aromatic molecules had no enough time to coalesce and be arranged orderly.⁸ As a result, the development of anisotropic structure was restricted and the formation of mesophase pitch was hindered. Although the modified materials treated by polyethylene glycol also contained some naphthenic structures which could moderate the carbonized reaction. But if there was an excess of alkyl chains, it would play leading roles during the thermal treatment, while the influence of naphthenic structures would be covered.^{24,25} So the mesophase pitch E4-MP presented an optical texture of

mosaic structure. In conclusion, the optical texture of T4-MP were more ordered than that of E3-MP, although T4-MP and E3-MP all displayed large domain structure, which indicated the better performance of tetrahydronaphthalene in modifying the feedstock compared to polyethylene glycol.

3.3 Softening point and carbon residue analyses of mesophase pitch

Table 5 listed the softening points and carbon residues of F-MP, T1-MP, T2-MP, T3-MP, T4-MP, E1-MP, E2-MP, E3-MP and E4-MP.

Table 5 Softening points and carbon residues of mesophase pitches

Sample	Softening point/°C	Carbon residue/wt%
F-MP	259	73.68
T1-MP	235	74.05
T2-MP	226	83.57
T3-MP	219	84.12
T4-MP	218	85.57
E1-MP	245	75.85
E2-MP	233	79.68
E3-MP	226	83.76
E4-MP	239	80.24

With the increase of tetrahydronaphthalene, the softening points of mesophase pitches decreased, while the carbon residues increased. This behavior could be explained by the hydrogen radicals generated by the modified materials with naphthenic structures during the polycondensation process.^{8,16} The hydrogen transfer reaction caused by the hydrogen radicals could alleviate the carbonization reaction and reduce the viscosity, so the reaction system maintained good fluidity. As a result, the softening points of mesophase pitches decreased with the increase of naphthenic structures. Meanwhile, the low molecular weight radicals produced during the pyrolysis process were easily to form polycyclic aromatic compounds with large molecular at low viscosity, which could reduce the spillage of components with low boiling points. So the carbon residues increased.

However, with the adding of polyethylene glycol, the softening points of mesophase pitches decrease first and then increased, while the variation tendency of the carbon residues

was just opposite to that of softening points. This phenomenon was due to the superabundance of alkyl chains in modified materials (when the amount of polyethylene glycol was 30 wt%), which accelerated the carbonized reaction. The fast reaction rate led to the excessive condensation, and then the softening points increased and the carbon residues decreased.

3.4 FTIR analysis of mesophase pitch

Fig. 5 presents the FTIR spectra of mesophase pitches (F-MP, T1-MP, T2-MP, T3-MP, T4-MP, E1-MP, E2-MP, E3-MP and E4-MP).

The absorption peaks of methyl $-\text{CH}_3$ (at 1380 cm^{-1}), alkyl C-H (at 2920 cm^{-1}) and aromatic C-H (at 3040 cm^{-1}) were presented in the spectra of mesophase pitches, which indicated that there were a certain amount of alkyl structures contained in mesophase pitches.⁸ The peak intensity ratio of isolated aromatic C-H to aromatic C=C reflected the condensation degrees of polycyclic aromatic hydrocarbons (PAH) was denoted as $\text{Abs}_{880}/\text{Abs}_{1600}$, and the aromatic index (I_{ar}) of mesophase pitch was defined as the formula: $\text{Abs}_{3040}/(\text{Abs}_{3040} + \text{Abs}_{2920})$.²² The calculated results suggested that $\text{Abs}_{880}/\text{Abs}_{1600}$ and I_{ar} of mesophase pitch decreased with the adding of tetrahydronaphthalene (showed in Table 6), which implied that the alkyl structures in mesophase pitches rose with the raising amount of tetrahydronaphthalene. However, with the increase of polyethylene glycol, the two parameters decreased first and then increased, which meant that the alkyl structures contained in mesophase pitches increased first and then decreased with the adding of polyethylene glycol.

The ortho-substitution index (I_{os}), represented the relative size of aromatic molecules, was calculated according to the formula: $\text{Abs}_{750}/(\text{Abs}_{750} + \text{Abs}_{815} + \text{Abs}_{880})$. The results of I_{os} of mesophase pitches are listed in Table 6. The date suggested that the relative sizes of mesophase molecules increased with the raising amount of tetrahydronaphthalene, while it increased first and then decreased with the adding of polyethylene glycol. This phenomenon could be explained by the increase of alkyl structures in modified materials. The existence of an abundant of naphthenic structure or a certain amount of alkyl chains could help to maintain good fluidity of the reaction system, which was beneficial for the growth of aromatic molecules, so the relative sizes of mesophase molecules increased with the

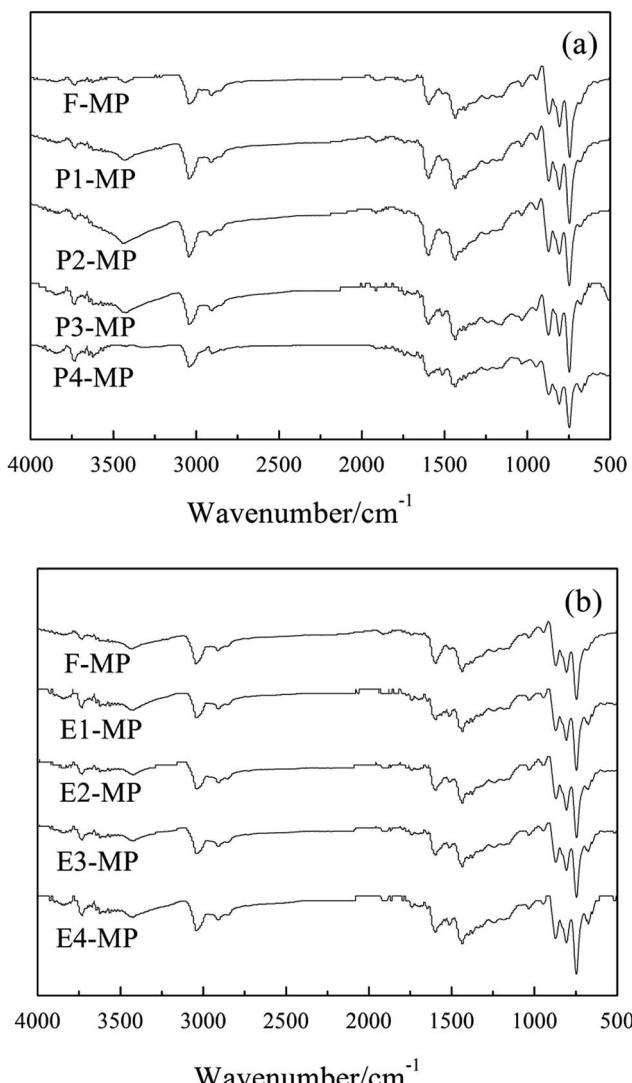


Fig. 5 FTIR spectra of mesophase pitches: (a) F-MP, T1-MP, T2-MP, T3-MP and T4-MP; (b) F-MP, E1-MP, E2-MP, E3-MP and E4-MP.

Table 6 The parameters $\text{Abs}_{880}/\text{Abs}_{1600}$, I_{ar} and I_{os} of mesophase pitches

Sample	$\text{Abs}_{880}/\text{Abs}_{1600}$	I_{ar}	I_{os}
F-MP	1.548	0.851	0.391
T1-MP	1.508	0.780	0.425
T2-MP	1.484	0.745	0.457
T3-MP	1.267	0.725	0.472
T4-MP	1.039	0.720	0.483
E1-MP	1.537	0.823	0.406
E2-MP	1.289	0.769	0.441
E3-MP	1.126	0.741	0.469
E4-MP	1.520	0.837	0.389



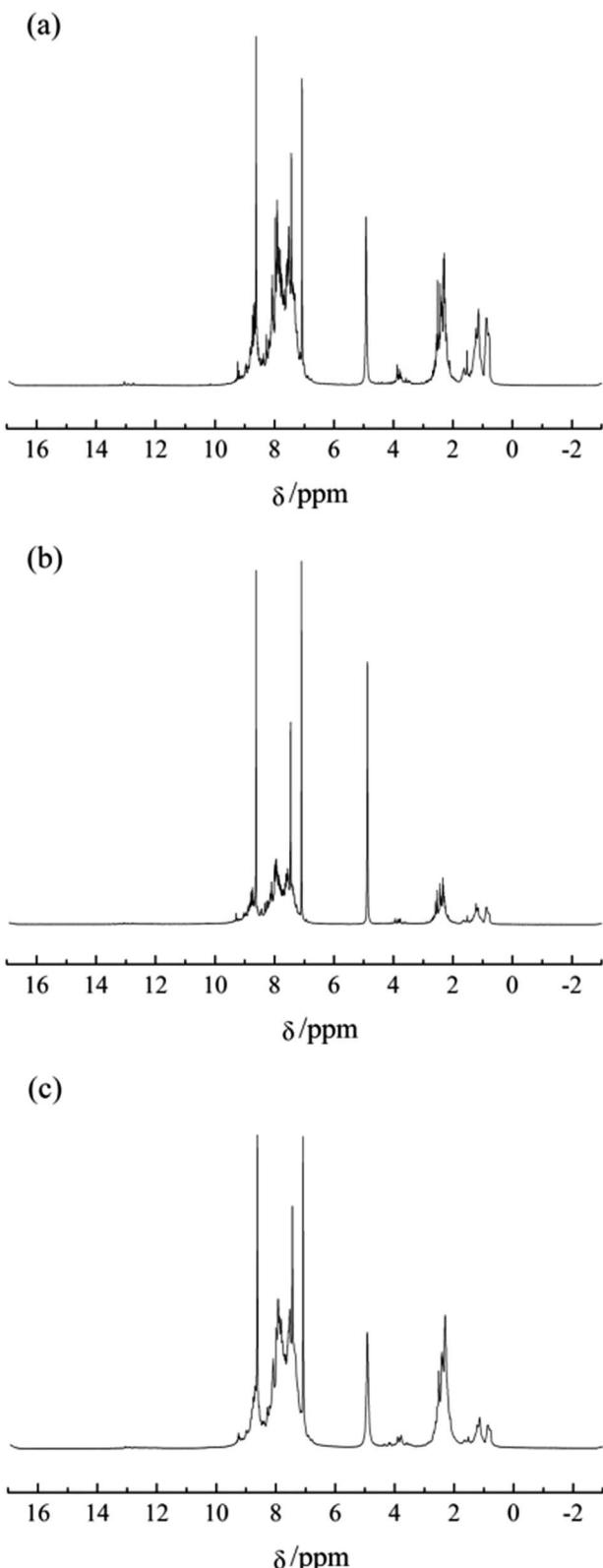


Fig. 6 ^1H NMR spectra of pyridine-soluble fractions of mesophase pitches. (a) F-MP-PS, (b) T4-MP-PS and (c) E3-MP-PS.

raising amount additives. But if there was an excess of alkyl chains (the amount of polyethylene glycol was 30 wt%), the high reaction rate and poor fluidity hindered the development of

mesophase molecules. Therefore, the ortho-substitution index of E4-MP decreased.

3.5 ^1H NMR analysis of mesophase pitch

The excellent mesophase pitches T4-MP and E3-MP were chosen to be analyzed by ^1H NMR. Fig. 6 present the ^1H NMR spectra of the pyridine-soluble fractions of F-MP, T4-MP and E3-MP (labeled as F-MP-PS, T4-MP-PS and E3-MP-PS, respectively) and Table 7 summarized the hydrogen distribution.

As shown in Table 7, the percent of H_{ar} hydrogens in T4-MP-PS and E3-MP-PS were higher than that in F-MP-PS obviously, which indicated that T4-MP-PS and E3-MP-PS possessed more alkyl structures than F-MP-PS. In contrast with F-MP-PS, the percent of H_{α} , H_{β} and H_{γ} in T4-MP-PS decreased, while the percent of H_{n} increased significantly, which demonstrated that the added alkyl structures in T4-MP-PS were almost naphthenic structures. Additionally, the percent of H_{α} and H_{n} in E3-MP-PS changed little compared with F-MP-PS, while the percent of H_{β} and H_{γ} increased. It implied that the incremental alkyl structures in E3-MP-PS were mainly alkyl chains. In conclusion, the naphthenic structure and alkyl chains contained in the modified materials partly remained in the mesophase pitches after the process of polymerization. Furthermore, considering the results of both optical texture and ^1H NMR analyses of mesophase pitch, T4-MP possessed more ordered optical texture than E3-MP, that is to say, the modification effect of the naphthenic structure was superior to that of alkyl chain.

3.6 XRD analysis of mesophase pitch

The X-ray diffraction patterns of the mesophase pitches F-MP, T4-MP and E3-MP are displayed in Fig. 7, and the microcrystalline parameters calculated from the XRD spectra are summarized in Table 8.

As shown in Fig. 7, the peaks of aromatic layers (at $2\theta \approx 25.6$) and crystal plane (at $2\theta \approx 43.0$) were exhibited in the patterns,²⁸ which suggested that the mesophase pitches F-MP, T4-MP and E3-MP were all well crystallized. Compared with F-MP, the interlayer spacings (d_{002}) of T4-MP and E3-MP were narrower, the stacking heights (L_c) were higher, the layer numbers (n) became larger, and the orientation degrees (O_g) were improved (shown in Table 8), which suggested that the mesophase pitches prepared by the modified materials became highly crystallized. Furthermore, the mesophase pitch T4-MP possessed better crystal structure than E3-MP: narrower interlayer spacing, higher stacking height, more aromatic molecular layers and

Table 7 Hydrogen distributions of F-MP-PS, T4-MP-PS and E3-MP-PS

Sample	Hydrogen contents/%				
	H_{ar}	H_{α}	H_{β}	H_{γ}	H_{n}
F-MP-PS	79.85	17.01	0.77	0.92	1.45
T4-MP-PS	74.32	14.34	0.64	0.86	9.84
E3-MP-PS	74.16	16.16	4.25	3.58	1.85

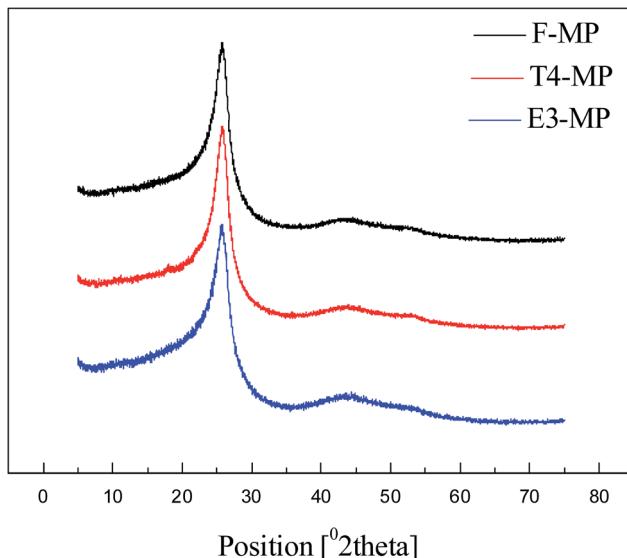


Fig. 7 XRD spectra of mesophase pitches.

improved orientation degree. This phenomenon implied that the feedstock modified by tetrahydronaphthalene was more beneficial to the preparation of mesophase pitch with ordered crystal structure compared to polyethylene glycol. It meant that the naphthenic structures in modified materials had a better effect in improving the crystal structure than alkyl chains.

3.7 Raman analysis of mesophase pitch

Fig. 8 exhibits the Raman spectra of mesophase pitches F-MP, T4-MP and E3-MP, and Table 9 lists the Raman parameters.

As shown in Fig. 8, the D peak (near 1360 cm^{-1}) and G peak (near 1580 cm^{-1}) represented the disordered carbon and the typical graphite lattices were displayed in the spectra of F-MP, T4-MP and E3-MP. In contrast to F-MP, the half-peak breadth (D) of T4-MP and E3-MP were narrower, and the I_D/I_G ratio became lower, which demonstrated that the crystalline imperfection of the mesophase pitches generated by modified materials decreased.^{8,26} Meanwhile, the crystal sizes (L_a) became larger, indicating the improvement of incipient graphitization degrees. This phenomenon could be explained by the increase of alkyl structures in the mesophase pitches. As previously stated, the presence of naphthenic structures and alkyl chains could reduce viscosity and improve rheological property of the reaction system, so the aromatic molecules had enough time to coalesce and be arranged orderly. As a result, the crystal

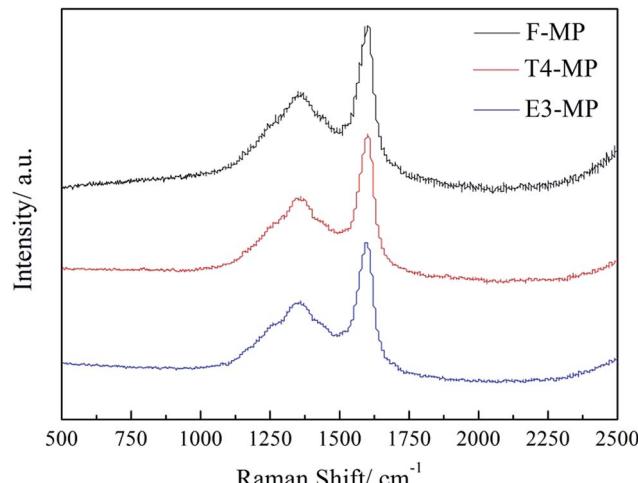


Fig. 8 Raman spectra of F-MP, T4-MP and E3-MP.

Table 9 Raman parameters of F-MP, T4-MP and E3-MP^a

Sample	D/cm^{-1}	I_D/I_G	$L_a (\times 10^{-2})$
F-MP	55	0.4561	1.2059
T4-MP	41	0.4001	1.3728
E3-MP	45	0.4092	1.3452

^a Note: D , half-peak breadth; I_D/I_G , intensity ratio of D peak to G peak; L_a , crystal size.

structure of mesophase pitches T4-MP and E3-MP were more ordered than that of F-MP. Furthermore, the mesophase pitch T4-MP possessed less crystalline imperfection and higher incipient graphitization degree than E3-MP, suggesting that the naphthenic structure were more helpful to improving the microcrystal structures of mesophase pitch compared to alkyl chains. It was consistent with the result of optical texture and XRD analyses.

In conclusion, the existence of an abundant of naphthenic structure or an appropriate amount of alkyl chains in the modified material contributed to the preparation of high quality mesophase pitch with large domain structure; low softening point, high carbon residue and ordered microcrystal structure.

4. Conclusion

The structural composition of feedstock has played a vital role in preparing mesophase pitch with high quality. The alkyl structures in modified materials treated by tetrahydronaphthalene and polyethylene glycol were mainly naphthenic structures and alkyl chains, respectively. Meanwhile, the mount of naphthenic structures and alkyl chains increased with the adding of modifying agents. Additionally, the mesophase pitches from modified materials possessed larger domain structure, lower softening point, higher carbon residue and more ordered microcrystal structure compared to the mesophase without treatment. Moreover, the improving effect of

Table 8 Microcrystalline parameters of mesophase pitches^a

Sample	$d_{002}/\text{\AA}$	L_c/nm	n	O_g
F-MP	3.72	2.28	7.69	0.902
T4-MP	3.47	3.07	10.87	0.967
E3-MP	3.56	2.76	9.01	0.943

^a Note: d_{002} , interlayer spacings; L_c , stacking heights; n , layer numbers; O_g , orientation degrees.



naphthenic structures in modified materials on the formation of mesophase was superior to that of alkyl chains. In short, an abundant of naphthenic structures or an appropriate amount of alkyl chains in the modified materials was helpful to the generation of mesophase pitch with high quality.

Conflicts of interest

There are no conflicts to declare.

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