

Modification of precursor pitch for general performance carbon fibre by blending naphthalene-derived isotropic and mesophase pitches

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Modification of an isotropic precursor pitch (IMP) for general performance carbon fibre (GPCF) was carried out by blending isotropic and mesophase pitches (IP and MP, respectively), both of which were synthesized from naphthalene using HF/BF₃ as catalysts because they carried a large amount of naphthenic hydrogens. Both IP and MP were miscible with IMP at temperatures higher than their softening points. The softening point of the blended pitch dropped remarkably, being lower than 200 °C with 40% IP. Such lower softening points made spinning much smoother. Modification also enhanced the stabilization reactivities of pitch fibre, the time required for the sufficient stabilization at 270 °C decreasing by 20 and 30 min by blending with 20% IP and 20% MP, respectively. The mechanical properties of the resultant carbon fibres were also improved.

1. Introduction

General performance carbon fibre (GPCF) has been commercialized from isotropic pitch (IMP) derived from coal tar pitch by air blowing, because of its low price and reasonable properties. However, spinnability, stabilization reactivity of the pitch fibre and the tensile strength of the resultant carbon fibre need to be improved. Basic properties of the isotropic pitch appear to originate from component molecules of the round disc, inheriting the structure of the parent coal tar pitch [1]. Such a structural characteristic causes several problems in the manufacture of pitch-based carbon fibre. One of the most concerning problems is the low strength of the as-spun pitch as well as of the resultant carbon fibre. The low reactivity of pitch fibre for the oxidative stabilization is another serious problem. A higher softening point of the precursor pitch tends to induce problems at spinning, although the stabilization is performed at higher temperature.

In previous papers [2–5], we reported the blending of precursor pitch with PVC (polyvinylchloride)-derived pitch, where the improvement with PVC pitch was very limited, because the main chain of PVC tends to be fissured to low molecular weight during heat treatment. Such problems can be solved by the blending of pitches synthesized from naphthalene using HF/BF₃ as the catalyst because synthesized pitches are very stable even at the spinning temperature and contain many naphthenic groups which are

very reactive against oxidative stabilization reaction [6–9].

In the present study, modifications of the particular precursor pitch for GPCF by blending synthesized isotropic and mesophase pitches were examined. The solubilities of molecular assemblies in the mesophase pitch were also examined in the isotropic pitch.

2. Experimental procedure

IMP was a coal tar-derived isotropic pitch which was commercially used for the production of GPCF. The additive pitches were isotropic (IP) and anisotropic (MP) pitches prepared from naphthalene using HF/BF₃ as catalysts [6–9]. Their properties are summarized in Table I.

The chemical structures of these pitches were analysed by field desorption (FD)-mass, and ¹H- and ¹³C-nuclear magnetic resonance (NMR) spectroscopies after solvent fractionation. The softening points of the starting and blended pitches were measured by a thermal mechanical analyser (Seiko SSC5200).

The pitches were spun into fibres of about 10 μm diameter under nitrogen pressure using a steel spinneret (0.3 mm diameter and $L/D = 2$).

Stabilization was carried out in air at 270 °C for various times at a heating rate of 5 °C min⁻¹. The stabilized fibres were further carbonized at 980 °C for 5 h at the heating rate of 50 °C min⁻¹.

TABLE I Some properties of used pitch

	Softening point (°C)	Solubility (wt %)			
		HS	HI-BS	BI-PS	PI
IMP	229	2	30	22	46
MP	189	3	53	6	38
IP	168	9	42	9	40

IMP, isotropic pitch produced from coal tar pitch; MP, mesophase pitch prepared using HF/BF₃; IP, isotropic pitch prepared using HF/BF₃.

3. Results

3.1. Chemical structure of original and additive pitches

The solubility and softening point of whole pitches are summarized in Table I. IMP showed a higher softening point and larger pyridine insoluble (PI) content than those of MP and IP. It should be noted that the synthesized pitches carried more hexane insoluble but benzene soluble (HI-BS) and less benzene insoluble but pyridine soluble (BI-PS) than IMP.

Fourier transform-infrared (FT-i.r.) spectra of the pitches are illustrated in Fig. 1. The bands at 2800–2980 cm⁻¹ and 1300–1450 cm⁻¹, which are ascribed to aliphatic C–H, were more intense in MP and IP than in IMP, indicating a higher content of naphthenic groups in the synthesized pitches. The intensities of the bands at 1600 cm⁻¹ (aromatic C=C) and 870–750 cm⁻¹ (aromatic C–H) of the additives were almost the same.

FD-mass spectra of BS fractions are illustrated in Fig. 2. Although these fractions have the same solubility, molecular weight distributions and peak positions were very different. MP showed a distribution in the larger molecular weight range while IMP showed it in the lower range. The intense peaks were located at about 560–630 cm⁻¹ with MP, 450–520 cm⁻¹ with IP and 320–370 cm⁻¹ with IMP, respectively, again indicating the highest molecular weight of MP.

Structural parameters of the BS fractions obtained by ¹H- and ¹³C-NMR spectra are summarized in Table II. Although MP exhibited 100 vol % anisotropy, the hydrogen distribution and *f_a* (aromaticity) value of its BS were almost the same as those of IP. The highest *H_{aro}* and *f_a* values of IMP may reflect its purely disc-like aromatic structure of its constituent molecules.

3.2. Some properties of blended pitches

The softening points of the blends of IMP with MP or IP are illustrated in Fig. 3. The softening point of IMP (229 °C) was lowered remarkably with increasing amount of additives, being lower than 200 °C with IP and 210 °C with MP, respectively, by blending with 40 wt %.

The optical textures of the blends from IMP with MP are shown in Fig. 4. The blend containing 20 wt % MP still maintained complete isotropy, indicating that the MP with 100% anisotropy is dissolved and dispersed in IMP to be isotropic. Many very small anisotropic spheres appeared on blending slightly

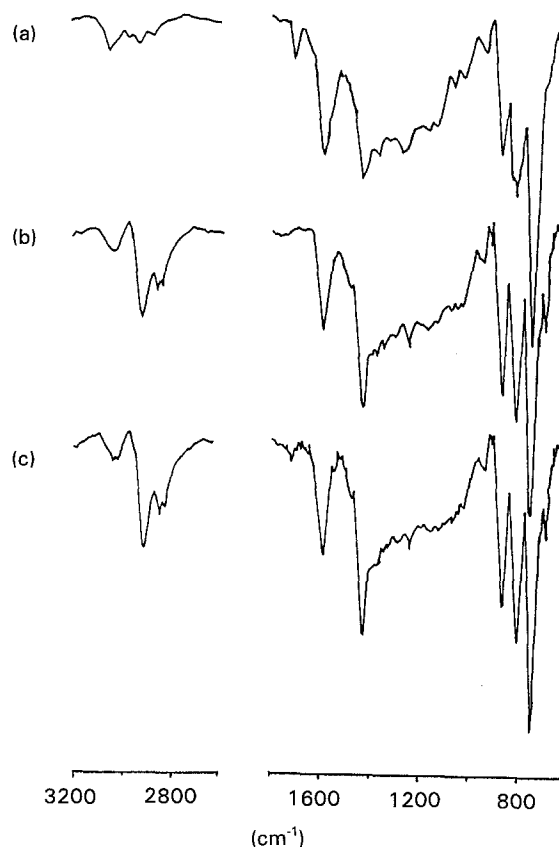


Figure 1 FT-i.r. spectra of the pitches. (a) IMP, (b) MP, (c) MP

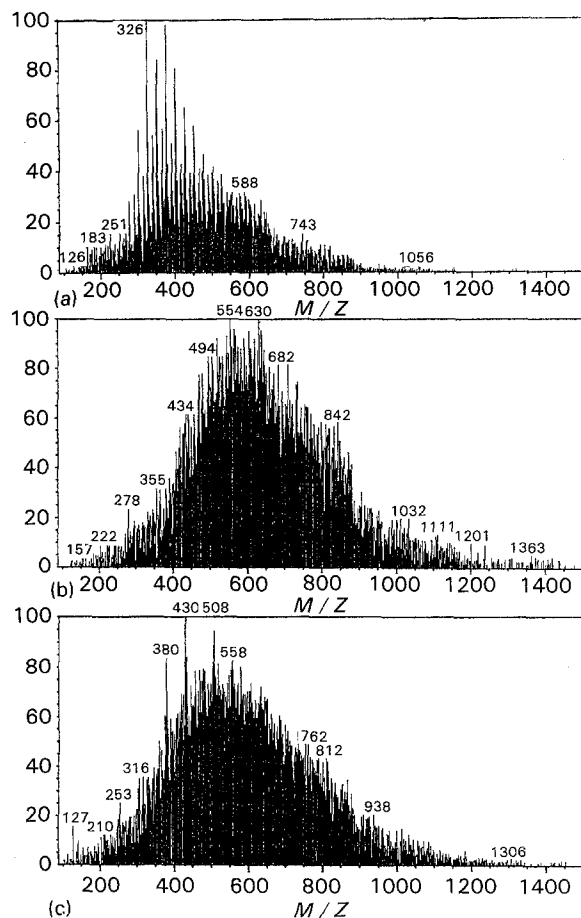


Figure 2 FD-mass spectra of the pitches. (a) IMP, (b) MP, (c) MP

TABLE II Structural parameters of BS fraction

	Hydrogen distribution				¹ H-NMR	¹³ C-NMR
	H _{aro}	H _α	H _β	H _γ	f _a	f _a
IMP	83	9	7	1	0.96	0.99
MP	51	28	20	1	0.83	0.87
IP	50	33	16	1	0.81	0.85

H_{aro}, aromatic hydrogen; H_α, hydrogen at α-position; H_β, hydrogen at β-position; H_γ, hydrogen at γ-position.

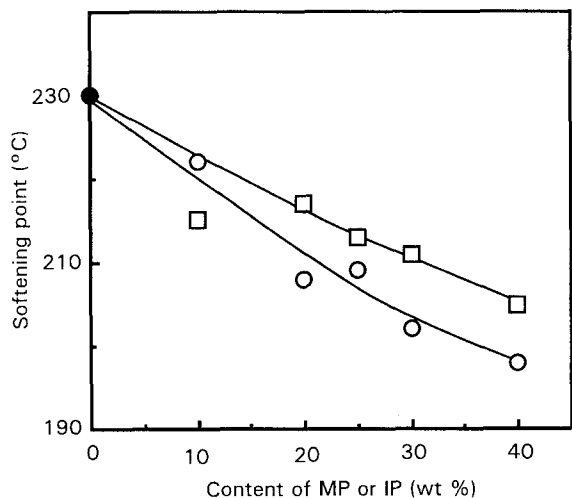


Figure 3 Softening point of the blended pitches with MP and IP. Blending temperature, 290 °C; time 10 min. (●) As-received IMP, (□) MP. (○) IP.

more MP (25 wt %). A further increase in the amount of MP increased the size and number of such spheres: 40 wt % MP increased the anisotropic content up to 17 vol %, again indicating that a large part of MP is still dissolved in IMP.

The high temperature fused state ¹³C-NMR spectra of MP and its blends with IMP are illustrated in Fig. 5. Two major peaks were found at about 130 and 170 p.p.m., both in the aromatic region, which are ascribed to aromatic carbon atoms unaligned and aligned with the external magnetic field, respectively [10, 11].

Although MP was 100 vol % optically anisotropic, it exhibited the resonance of unaligned aromatic carbons. The resonance of the aligned carbon in MP disappeared when 20% MP was blended with IMP. A very broad peak of low intensity appeared at 170 p.p.m. by the addition of 40 wt % MP. The relative resonance intensity was 17%.

3.3. Spinning and stabilization properties

The most suitable spinning temperatures of the blends are illustrated in Fig. 6. The suitable spinning temperature of the blends with IP was lowered in the same manner as its softening point. In contrast, it was rather difficult to spin the fibre from the blends with as-received MP at around 290 °C except the blend with 5 wt % addition, because frequent gas evolution from part of the HS in MP at the spinning temperature interrupted the smooth spinning. The heat treatment

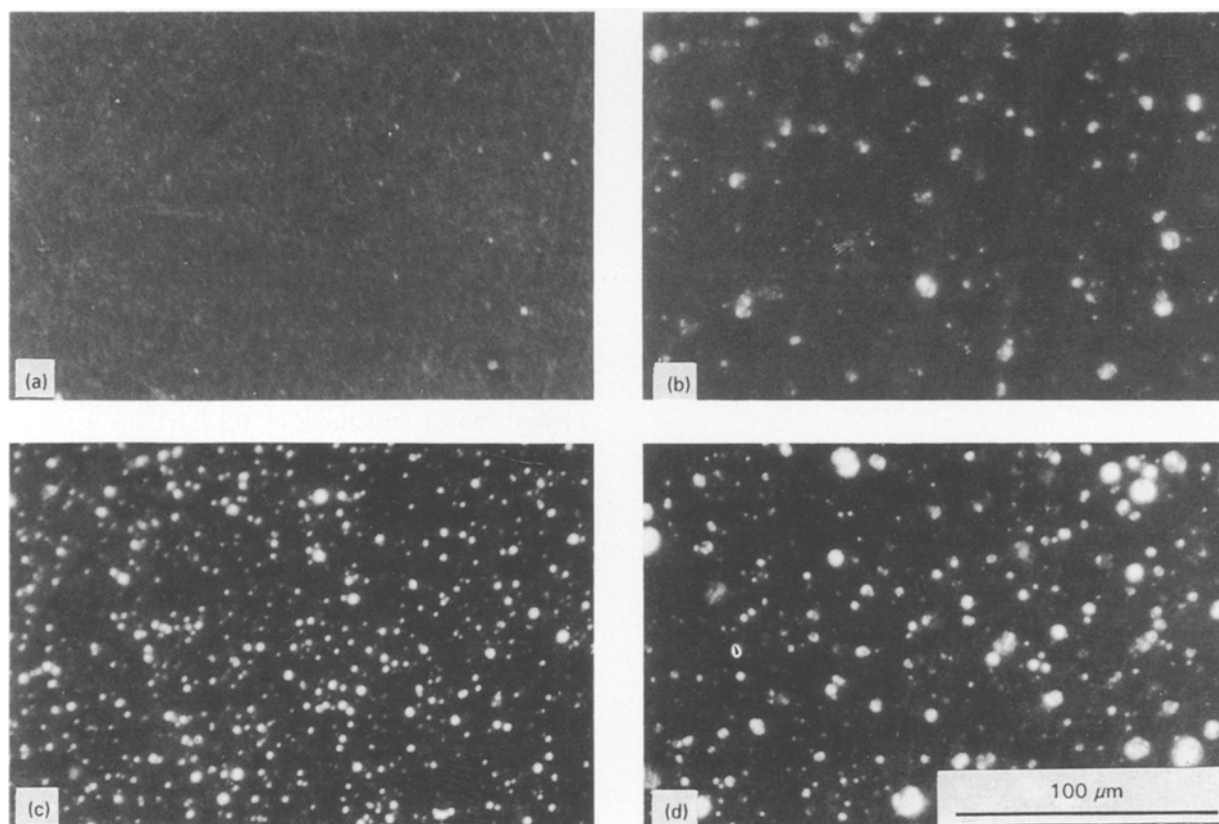


Figure 4 Optical texture of blended IMP with MP. MP (wt %): (a) 20, (b) 25, (c) 30, (d) 40.

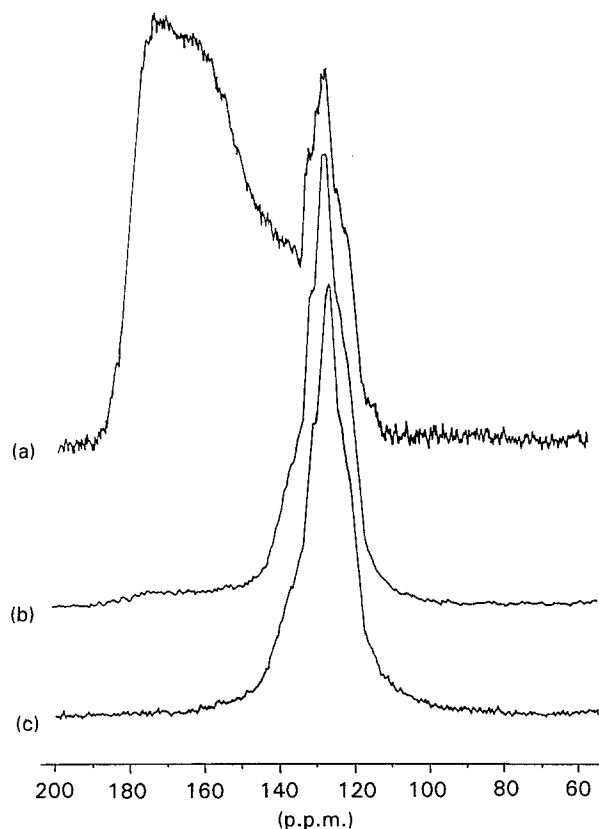


Figure 5 High-temperature ^{13}C -NMR spectra of MP and blends. (a) MP, (b) 20 wt % MP. (c) 40 wt % MP.

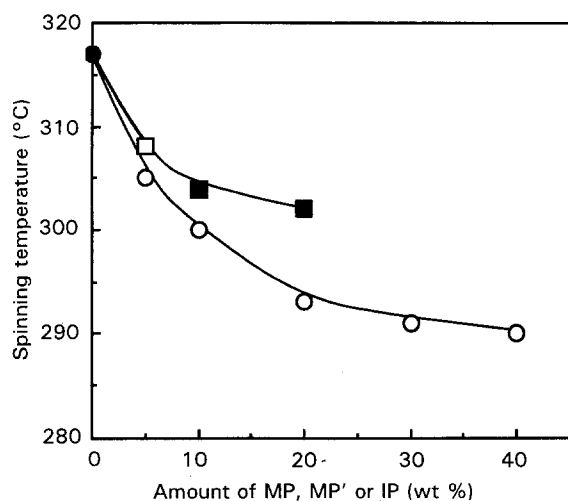


Figure 6 Suitable spinning temperature of the blends. (●) as-received IMP, (□) MP, (○) IP, (■) MP'.

of MP at 290°C for 1 h under 1.0 torr (MP') was effective in removing the volatile matter, smooth spinning being achieved even at 20 wt % addition at a lower spinning temperature of 300°C . Further increase at MP' blending made spinning difficult. A large number of anisotropic spheres found in the isotropic matrix when the blended pitch was cooled (Fig. 4) may hinder spinning.

The times required for complete stabilization of the pitch fibres spun from the blends are plotted in Fig. 7, where stabilization was carried out in air at 270°C at a heating rate of 5°C min^{-1} . The pitch fibres from the blends were stabilized much faster than that from

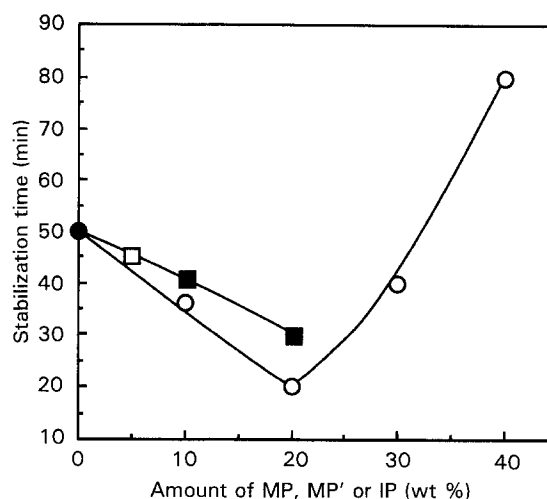


Figure 7 Stabilization time of the pitch fibre from the blends. Heating rate 5°C min^{-1} , stabilization temperature 270°C . (●) As-received IMP, (□) MP, (○) IP, (■) MP'.

IMP, stabilization times decreasing to 30 min for MP' and 20 min for IP with 20 wt % addition. A further increase in the amount increased the stabilization time, thus lowering the softening point limiting the heating rate and temperature for the stabilization.

The oxygen up-take during the stabilization is plotted in Fig. 8, where the stabilization was carried out at 300°C at a heating rate of 2°C min^{-1} . The pitch fibres from the blends showed higher reactivity against oxygen than that from IMP. Such higher reactivities were ascribed to naphthenic hydrogens in IP and MP.

3.4. Tensile strength of the resultant carbon fibre

The effects of blending on the tensile strength of resultant carbon fibres are illustrated in Fig. 9. The tensile strength strongly depends on the amount of added pitch. Higher strength was obtained by the addition of 5 wt % MP where the stabilization was carried out for 2 or 3 h. Further increase of MP decreased the strength; however, the addition of 20 wt % MP still provided higher strength than IMP alone.

4. Discussion

Typical model structures of BS fractions estimated based on the structural analyses are illustrated in Fig. 10. Among the BS fractions of the pitches, the aromaticity of IMP is very high and its molecular weight is the lowest. Both MP and IP contain many naphthenic groups. Such structures of the synthesized pitches can successfully modify the properties of IMP for GPCF by blending. The blended pitch at suitable ratios showed lower softening point and improved spinnability than IMP. Stabilization time can be reduced significantly by blending with MP or IP. The naphthenic groups can trigger the stabilization of the aromatic-rich structure of IMP. Such a favourable effect of blending is achieved by homogeneous mixing of both pitches due to the high ability of

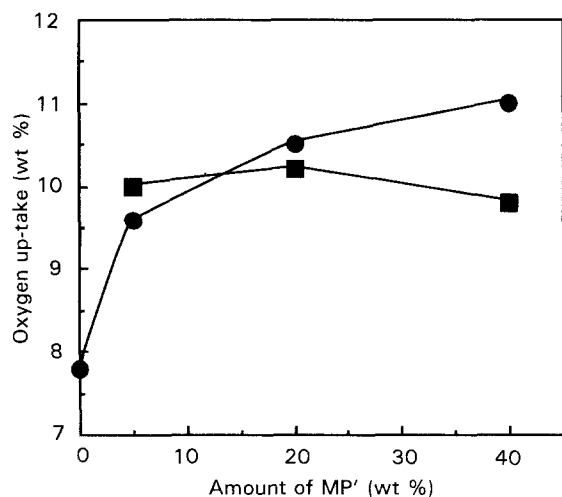


Figure 8 The amount of oxygen up-take during stabilization. Stabilization conditions: heating rate $2^{\circ}\text{C min}^{-1}$; temperature 300°C : Holding time (●) 3.0 h, (■) 2.0 h

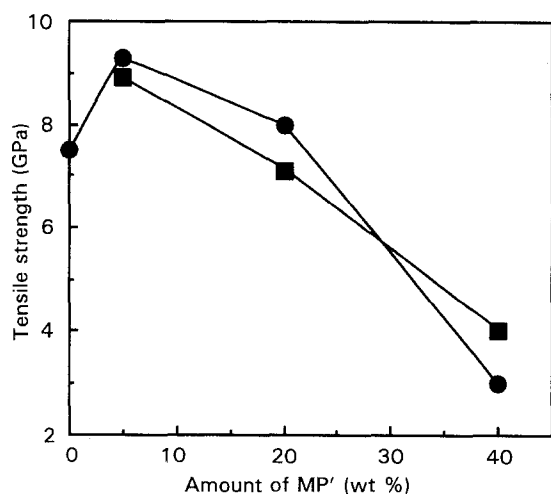


Figure 9 Tensile strength of carbon fibre from the blends. Stabilization conditions: holding time (●) 3.0 h, (■) 2.0 h. Carbonization conditions: heating rate $50^{\circ}\text{C min}^{-1}$, temperature 980°C .

naphthenic-rich pitches to dissolve in the highly aromatic matrix. Some hydrogen transfer may occur from naphthenic-rich pitch to the aromatic rings of IMP to enhance the mutual solubility of pitch as well as the stabilization reactivity of the latter component. The blending may lead to the condensation among the pitch components, increasing the molecular size. Such enlarged molecules may allow better alignment along the fibre axis during spinning and may link together smoothly during the early stage of carbonization to improve further the axial alignment, thus reducing the number of defects at a molecular level. All these improvements by blending the synthetic pitch contribute to the better tensile strength of the resultant carbon fibre. The shorter stabilization time achieved by blending is another merit, which reduces the cost of the carbon fibre considerably. Further study to deter-

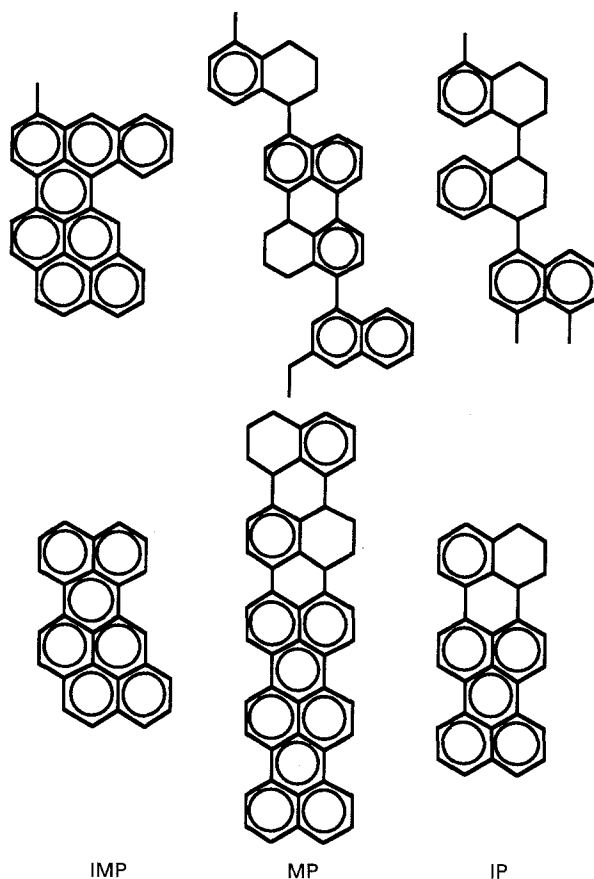


Figure 10 Model structures of BS fractions.

mine the optimum spinning and stabilization conditions may produce a carbon fibre of tensile strength higher than 2 GPa from inexpensive coal tar with the aid of synthetic pitches at reasonable cost.

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