Investigation of the Early Stage of Carbonization for Petroleum Pitch By Means of High-Temperature ^{1}H-NMR and ESR

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The early stage of carbonization of petroleum pitches has been investigated by in-situ high-temperature ^{1}H-NMR and ESR spin probe. Well resolved ^{1}H-NMR spectra through out the pyrolysis of pitches provided detailed information about mesophase formation. The ESR spin probe method also provided useful information about mesophase generation during the cooling process.

Introduction

High-temperature ^{1}H-NMR[1-4] and ESR spin probe[5-8] methods have been recognized as useful tools for obtaining information about molecular motion and chemical change in the early stage of carbonization of coals and petroleum pitches.

The purpose of this study is to measure ^{1}H-NMR spectra of several petroleum pitches as a function of temperature and to correlate these with mesophase formation in terms of changes in the line width and hydrogen aromaticity.

The nucleation of mesophase embryo and mesophase formation during the cooling process is also discussed in terms of ESR spin probe results.

Experimental

Table 1 shows the characteristics of the samples used in this experiment.

A Bruker high-temperature probe operating at 36.4MHz was used for measuring high-temperature ^{1}H-NMR[1]. In order to improve the resolution of the spectrum at higher temperatures, a home-built shim system[4] was used.

Table 1. Elemental analysis and softening point of pitches.

Sample	Elemental analysis (wt%) C	H	N	Softening point (°C)
Pitch A	91.9	5.4	0.0	115
Pitch B	93.3	6.2	<0.2	102
Pitch C*	92.6	6.5	<0.2	80

* made from Pitch B by hydrogenation

Samples were heated at a rate of 5°C/min in the high-temperature probe under nitrogen gas flow.

High-temperature ESR spectra were obtained using a Varian Model E109 ESR with cylindrical high-temperature cavity.

Vanadyl tetraphenyl porphyrin (VTPP) was doped into the pitch samples as a spin probe. The concentration of the vanadium metal component of VTPP was about 1000 ppm. Samples were heated from room temperature up to 415°C at a rate of 5°C/min, held for 5 mitutes, and then cooled at a rate of 1°C/min within the high-temperature probe under nitrogen gas flow. The ESR spectra of V were monitored during the heating/cooling process.

Results and Discussion

In Figure 1 the temperature dependence of the half-width ($\Delta H1/2$) obtained from high temperature ^{1}H-NMR spectra is shown for pitch A, B and C. With increasing temperature, $\Delta H1/2$ shows an intermediate maximum at about 420°C and 430°C for pitch A and B respectively, while no maximum was observed for pitch C. This intermediate maximum may correspond to a rheological phenomenon due to a geometric change in the mesophase/matrix.

Observation of quenched specimens by optical microscope shows that the appearance of mesophase spheres takes place in the vicinity of 440°C for pitch A.

Figure 2 shows the change in ESR spectra of VTPP in Pitch A during heating and cooling. The anisotropic lines become weak as the temperature rises, and then the eight isotropic lines begin to appear.

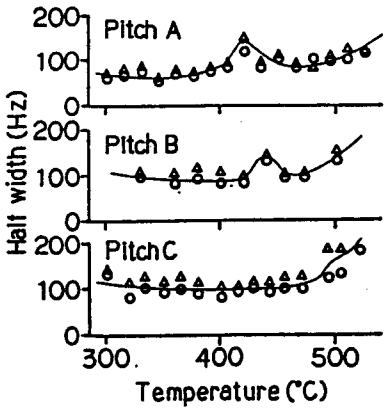

Fig. 1 Temperature dependence of half width of Pitch A, B and C.
(Δ Aliphatic hydrogen, o Aromatic hydrogen)

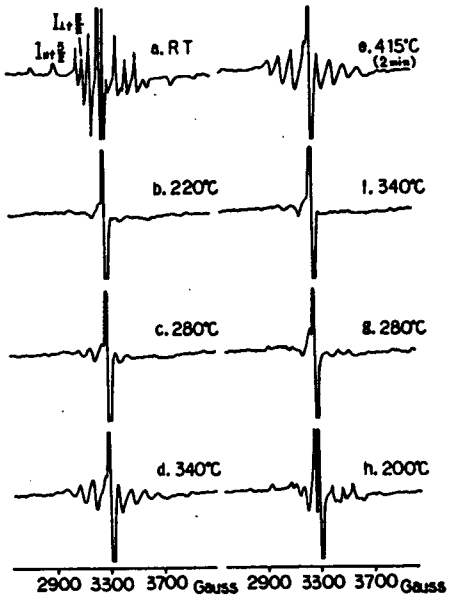

Fig. 2 Change in ESR spectra of VTPP in Pitch A during heating and cooling.

On cooling the specimen, the anisotropic spectrum reappears in the vicinity of 280°C and becomes strong at 200°C. Pitch B shows similar behavoir to that of Pitch A, but Pitch C shows no anisotropic spectrum during cooling to 200°C.

The rotational correlation times (τ_c) for these pitches were calculated from the isotropic signals of VTPP[6] and are shown in Figure 3. The correlation time for each sample decreases with increasing temperature. The minimum of (τ_c) was observed for pitch A and B at about 415°C.

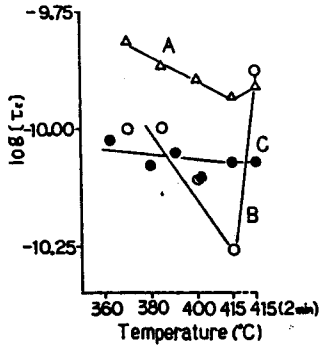

Fig. 3 Temperature dependence of correlation times (τ_c).
(Δ Pitch A, o Pitch B, ● Pitch C)

This temperature seems to correlate with the temperature maximum for ΔH1/2, obtained from high temperature NMR.

Large mesophase spheres are observed for Pitch A and Pitch B quenched at 200°C after slow cooling, but no mesophase was observed for any of the three pitches when they were quenched to room temperature after being held at 415°C for 5 minutes.

Conclusion

^{1}H-NMR and ESR spin probe techniques were found to be useful tools for direct monitoring of mesophase generation during the heating and cooling processes.

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References

1) T. Yokono, K. Miyazawa, Y. Sanada and S. Shimokawa, Fuel, 58, 239(1979).
2) K. Miyazawa, T. Yokono, Y. Sanada, E. Yamada and S. Shimokawa, Carbon, 19, 143(1981).
3) T. Yokono, T. Obara, Y. Sanada and K. Miyazawa, Carbon, 22, 169(1984).
4) S. Shimokawa and E. Yamada, Joint ACS/JCS Honolulu meeting, Polymer Reprints 20, 683(1979).
5) E. C. Tynan and T. F. Yen, Fuel, 43, 191(1969).
6) Y. Yamada, K. Ouchi, Y. Sanada and T. Sohma, Fuel, 57, 79(1978).
7) K. Shibata, H. Kakiyama, Y. Sanada and T. Sohma, Fuel, 57, 651(1978).
8) T. Yokono, N. Oka and Y. Sanada, Carbon in Press, Feb(1985).