

Temperature Dependence of ^1H NMR Absorption in Coal and Pitch

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Introduction

Many kinds of reactions such as pyrolysis, depolymerization, condensation occur simultaneously in complicated way when coal and tar pitch are heated over temperature range from 350°C to 500°C. In order to understand the processes of coal liquefaction and coal carbonization, it is important to clarify the characteristics of reaction behaviors for coal and tar pitch over the temperature range.

It is well known that pitch, solvent refined coal (SRC) and coking coal produce various kinds of mesophase at the early stages of carbonization [1-3]. The mechanisms of many chemical reactions and physical transformations relating to mesophase formation are studied by quenching techniques. Such research techniques as polarized light-microscopy and so on can be extremely fruitful. On the other hand, direct observation of phenomena at reaction temperatures may yield more easily interpretable or more relevant results. Line shape of NMR corresponding to mobility of molecule and/or segment in coal and tar pitch have been measured at the temperature range of mesophase formation.

No report has been appeared on direct measurement of change of hydrogen aromaticity (f_{Ha}) at higher temperature occurring pyrolysis and carbonization. This paper deals with observation of resolved NMR spectra corresponding to aromatic and aliphatic protons at high temperatures in a tar pitch. High resolution NMR spectra for thermally decomposed polyvinyl chloride were observed by S. Shimokawa et al. [4] over the temperature range from 350°C to 450°C using the same apparatus at Hokkaido University.

Experimental

The experiments were done by using a Bruker Sxp 4-100 pulsed Fourier transform (FT) spectrometer with a high temperature probe and an improved JEOL 3H electromagnet (0.88T) with a 60 mm gap operating at 36.4 MHz for the ^1H NMR. In order to improve the resolution of a spectrum at high temperatures, a home-built shim system was used [4]. Outlines of the high temperature probe and flowing gas system are illustrated in Fig. 1. The samples as received were heated in the high temperature probe and NMR spectra were obtained simultaneously. No heat-treatment was done before measurements. Kureha pitch was heated at 10°C min⁻¹ and the others were heated at 5°C min⁻¹ to various given temperatures under nitrogen gas flushing. In the case of the resolved NMR spectra for ethylene tar pitch, the heating rate employed was 2°C min⁻¹. Characteristics of all samples so far studied are shown in Table 1.

Results and discussion

Temperature dependence of molecular and/or segmental motion

Representative proton NMR spectra for coals and solvent extracts from coal are shown in Fig. 2. Apparently, there is no structure in the lines. Increasing temperature produces changes in the spectra. In order to discuss the broadening behavior quantitatively, the values of the line widths at half-height ($\Delta H_{1/2}$) were utilized. Temperature dependence of $\Delta H_{1/2}$ is shown in Fig. 3. It is obvious that there are three different groups with respect to temperature dependence of $\Delta H_{1/2}$. The value of $\Delta H_{1/2}$ of the first group to which Taiheiyo coal belongs decreases and then increases rapidly with increasing temperature. The behavior of $\Delta H_{1/2}$ of the second group, Yubarishinko coal and β -component (pyridine soluble, chloroform insoluble fraction of a coal [5]) of Yubarishinko coal, resembles that of the first group, but the curve of $\Delta H_{1/2}$ is shifted to higher temperatures. The third group, which includes γ -component (pyridine soluble, chloroform soluble fraction of a coal [5]) of Yubarishinko coal, coal tar pitch and ethylene tar pitch, indicates that the values of $\Delta H_{1/2}$ remain small over

a wide temperature range. This suggests that the molecules and/or segments in them are mobile throughout the temperature range.

The carbonization process at low temperatures has been studied by the method of polarized-light microscopy. The formation of low temperature carbons by solidification from a liquid phase proceeds through the separation of an optically anisotropic mesophase.

Optically anisotropic textures of mesophase from the samples heat-treated at the early stages of carbonization are classified into five types corresponding to isotropic, fine mosaic, coarse mosaic, fibrous and domain. It has been found that there is a close relation between the spin-lattice relaxation time, T_1 , observed with pulsed FT NMR at room temperature and microstructure of mesophase, transformed from the parent matrix of coal. That is, the longer the relaxation time is, the more sufficient the growth of mesophase from the matrix occurs as shown in Table 1. The parent materials, which give the fibrous/domain texture at the early stages of carbonization, have the longest relaxation time so far as being described in the table. There is also an excellent relation between the microstructure of mesophase and the temperature dependence of $\Delta H_{1/2}$. The minimum value of the line width at half-height with respect to the temperature dependence of $\Delta H_{1/2}$ is expressed as $\Delta H_{1/2, \min}$ and used for characterization of mesophase texture. $\Delta H_{1/2, \min}$ of isotropic mesophase is larger than that of coarse or fibrous/domain mesophase and the temperature of isotropic mesophase corresponding to $\Delta H_{1/2, \min}$ is lower than that of fine mosaic mesophase. The values of $\Delta H_{1/2}$ in coarse mosaic or fibrous mesophase keep small over a wide temperature range (see Fig. 3). But no distinction was observed between coarse mosaic and fibrous textures concerning the broadening behavior of NMR.

Regarding the concentration of free radicals and the line width, these values remain almost constant up to about 400°C for coals of different rank [6]. Therefore, it seems that the contribution of free radicals on the NMR line width is not so important as that of the proton dipole-dipole interaction.

At higher temperatures we estimate the value of T_1 following equation,

$$t = T_1 \ln 2$$

where t is the time at the amplitude of the Free Induction Decay (FID) following the 90° pulse being equal to zero. Pulse sequence used was 180°- τ -90° in this experiment.

Fig. 4 shows the relation between the T_1 of ethylene tar pitch and the inverse of temperature. T_1 of ethylene tar pitch has the value of 400 ms at room temperature. It decreases with the increase of temperature, and reaches a minimum value at about 150°C. As is shown in the figure, T_1 has a maximum value of 190 ms at 340°C, and decreases rapidly with the increase of temperature.

It is clearly marked that the aromaticity of ethylene tar pitch increases with increase of temperature at 340°C and the formation of mesophase for the sample heat-treated becomes observable by an optical microscope. Rotational correlation time for aromatic lamellae, which are stacking parallel each other in the mesophase, is long due to being in rigid state. Accordingly T_1 becomes short. However, more detailed discussion will be made with further experiments.

NMR line simulation by means of computer

A proton NMR spectrum from Kureha pitch at 450°C (15 min) (a) and a comparison of the experimentally observed spectrum with a computer simulated spectrum (b) are illustrated in Fig. 5. The spectrum (a) contains considerable intensity in the wings of the line, and the ratio of the width at one-eighth height to that at one-half height, indicated by the symbol $R(8/2)$, is 6.4. The ratio for a pure Lorentzian line is 2.64 and for a pure Gaussian line is 1.73 [7]. By means of computer simulation the NMR line for the mesophase in Kureha pitch is composed of at least three different components, i.e. one Gaussian component with value of proton spin-spin relaxation time $T_2=7$ microseconds and two Lorentzian components with those of $T_2=210$ and 636 microseconds at 36.4 MHz, respectively. The fractions are also estimated as 0.85, 0.05 and 0.10, respectively. Kureha pitch at the early stages of carbonization contains 85 percent rigid structures from the view point of general NMR behavior [8].

In some liquid crystal systems broad partially resolved spectra with little structure attributed to proton dipole-dipole interaction have been observed [9-11]. On the other hand, such spectra were not observed in this study, so that the

ordering parameters of the samples employed would be expected to be very small. This result is compatible with that of ESR study reported by Yamada et al. [12].

Resolved NMR spectra at thermal decomposition temperature

In order to improve the resolution at higher temperature, a home-built shim system was attached with the magnet of NMR spectrometer. Typical ^1H NMR spectra for ethylene tar pitch are shown in Fig. 6. On heating at about 84°C , a broad resonance with no resolved structure becomes observable. And then at about 123°C , the NMR spectrum shows two discrete lines apparently, 200 Hz apart. That is, the lines correspond to the resonance due to aromatic and aliphatic protons. Assignment of the two peaks was done by comparing with the ones of a pure compound, acenaphthylene, which has the value of 0.75 hydrogen aromaticity (f_{Ha}). At about 208°C , the NMR spectrum becomes narrow and separately due to the rapid tumbling of molecule in ethylene tar pitch. This suggests that the molecules exhibit the random motion similar to that in isotropic solution and the value of the dipolar tensor over all orientation in them is almost zero in the vicinity of this temperature. However, fine structures due to the protons attached to α , β and γ carbons refer to aromatic rings were not able to observe at the higher temperatures, because of superposition of protons having various chemical shifts.

The intensity of aliphatic protons is higher than that of aromatic ones up to 208°C , at which the intensity change is observable. The values of f_{Ha} are able to elucidated from the intensity of the splitted spectra. However, two lines merge and broaden raising at about 430°C . Heating of the specimen at higher temperatures accelerates the degree of broadening of the spectrum. Therefore, it is difficult to observe the spectrum in the range of a usual high resolution NMR sweep width.

The spectrum obtained with a wider sweep width (25kHz) are shown in Fig.

7. For the spectrum in the figure, the ratio of the width at one-eighth height to that at one-half height, indicated by the symbol $R(8/2)$, is 7.0. This line shape is designated as "Super Lorentzian" [13] which contains considerable intensity in the wings of the line. After the measurement of the NMR spectra at 470°C , the sample was immediately quenched to room temperature and observed by polarized light-microscopy. And it was confirmed that the bulk mesophase was produced at 470°C .

When a magnetic field is applied, it is known that the direction of alignment of c-axes of mesophase spherules is aligned perpendicular to that of the magnetic field by interacting magnetic anisotropy of polycondensed aromatic molecules with the magnetic field applied [14]. On heating of ethylene tar pitch beyond 430°C in a magnetic field, a dipolar tensor is only partially averaged due to less chaotic molecular motion in a magnetic field. Resulting line becomes broad but is not as broad as solid. The structure of the mesophase produced in an NMR magnetic field is more rigid than that of isotropic liquid.

Table 2 summarizes range of sweep width for various NMR type at 36.4 MHz of resonance frequency. Generally, the sweep width of broad line NMR is the order of $10^5 \sim 10^6$ Hz, while that of high resolution NMR is about 10^3 Hz at 36.4 MHz for a proton. But the NMR spectrum of the mesophase obtained from ethylene tar pitch shown in Fig. 7 was swept over 2.5×10^4 Hz. Thus, the sweep width of the NMR spectrum for the carbonaceous mesophase is intermediate between those of broad line NMR and high resolution NMR. It seems that the result is supported by that obtained by J. J. Fink et al. [15]. They have measured the line width of 2.3×10^{-4} to 3.1×10^{-4} T for conventional nematic and smectic liquid crystals.

Conclusion

It could be concluded from the above results that the materials which give spherical mesophase on heating show a narrowing of the NMR with increasing temperature which corresponds to so-called softening and plastic stages. Moreover, the degree of motional narrowing of the proton NMR spectra reflects the degree of fluidity at the plastic stage. The temperature dependence of hydrogen aromaticity would be monitored directly by using the NMR high temperature technique.

Chemical reactions such as pyrolysis, depolymerization, condensation could be clarified. Moreover, application of the technique seems to be promising in the mechanism of coal liquefaction as well as that of mesophase formation.

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References

- [1] J. D. Brooks and G. H. Taylor, *Carbon*, 3, 185 (1965)
- [2] H. Honda, H. Kimura, Y. Sanada, S. Sugawara and T. Furuta, *Carbon*, 8, 181 (1970)
- [3] J. Dubois, C. Agache and J. L. White, *Metallography*, 3, 337 (1970)
- [4] S. Shimokawa and E. Yamada, *J. Phys. Chem.*, submitted
- [5] R. V. Wheeler and M. J. Burgess, *J. Chem. Soc.*, 649 (1911)
- [6] J. Smidt and D. W. van Krevelen, *Fuel*, 38, 355 (1959)
- [7] C. P. Poole, Jr. and H. Farach, *The Theory of Magnetic Resonance*. John Wiley & Sons, Inc. (1972)
- [8] A. Abragam, *The Principles of Nuclear Magnetism*, Clarendon Press, Oxford (1961)
- [9] A. Saupe and G. Englert, *Phys. Rev. Letters*, 11, 462 (1963)
- [10] K. R. K. Easwaran, *J. Mag. Res.* 9, 190 (1973)
- [11] J. C. Rowell, W. D. Phillips, L. R. Melby and M. Panar, *J. Chem. Phys.*, 43, 3442 (1965)
- [12] Y. Yamada, K. Ouchi, Y. Sanada and J. Sohma, *Fuel*, 57, 79 (1978)
- [13] K. D. Lawson and T. J. Flautt, *J. Phys. Chem.*, 72, 2066 (1968)
- [14] L. S. Singer and R. T. Lewis, 11th Biennial Conference on Carbon, Gatlinburg, Tennessee, Prepring, CG-27 (1973)
- [15] J. J. Fink, H. A. Moses and P. S. Cohen, *J. Chem. Phys.*, 56, 6198, 1972
- [16] T. Yokono, K. Miyazawa and Y. Sanada, *Fuel*, 57, 555 (1978)
- [17] T. Yokono and Y. Sanada, *Fuel*, 57, 334 (1978)

Table 1
Characteristics of samples used

Sample	weight % (d.a.f.)					f_a 1)	T_1 (ms) 2)	Optical texture in carbonized coal
	C	H	N	S	O			
Taiheiyō coal	77.0	6.0	1.4	0.1	15.5	0.70	18	isotropic
Hongei coal	93.1	3.2	1.0	2.7	-	0.70	58	isotropic
Miike coal	83.5	6.2	1.2	1.8	7.3	-	421	fine mosaic
Yubarishinko coal	86.6	5.9	2.0	0.3	5.2	0.80	438	fine mosaic
β-component of Yubarishinko coal	82.2	5.7	2.2	-	-	0.78	531	fine mosaic
γ-component of Yubarishinko coal	87.8	7.0	1.5	-	-	0.80	719	coarse mosaic
Kureha pitch	95.2	4.2	0.1	0.2	0.3	0.86	952	fibrous/domain
Ethylene tar	94.3	5.5	0	0.1	0.1	0.78	1103	fibrous/domain
Coal tar pitch	92.1	4.8	1.3	0.3	1.5	0.83	1560	fibrous/domain

1) values obtained from proton spin-spin relaxation time at -100°C [16]

2) proton spin-lattice relaxation time [17]

Table 2
 Range of sweep width for various NMR at 36.4 MHz of
 resonance frequency [$H_0=0.88T$]

NMR	Range of sweep width (Hz)
High resolution	10^3
Intermediate	10^4
Broad line	$10^5 \sim 10^6$

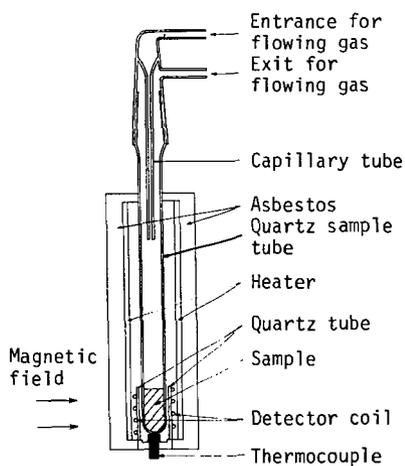


Fig. 1 Outlines of the high temperature probe and flowing gas system.

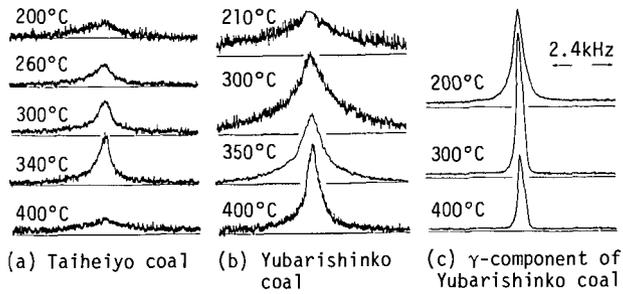


Fig. 2 Proton NMR spectra of Taiheiyo coal (a), Yubarishinko coal (b) and γ -component of Yubarishinko coal (c) at high temperatures.

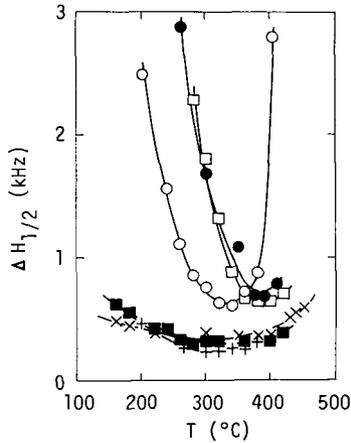


Fig. 3 Temperature dependence of the line width at half-height ($\Delta H_{1/2}$): \circ Taiheiyo coal, \bullet Yubarishinko coal, \square β -component of Yubarishinko coal, \blacksquare γ -component of Yubarishinko coal, $+$ Coal tar pitch and \times Ethylene tar pitch.

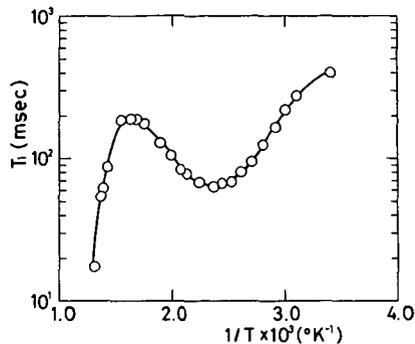


Fig. 4 Temperature dependence of spin-lattice relaxation time (T_1) of ethylene tar pitch.

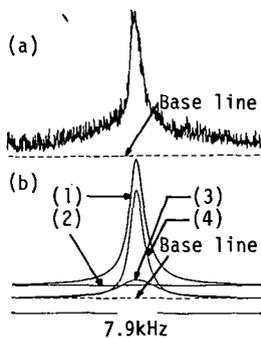


Fig. 5 A proton NMR spectrum of Kureha pitch at 450°C (for 15 min) (a) and a comparison of the experimentally observed spectrum with a computer simulated spectrum (b): (1) Total simulated curve, (2) Gaussian component with $T_2=7 \mu\text{s}$, (3) Lorentzian component with $T_2=210 \mu\text{s}$ and (4) Lorentzian component with $T_2=636 \mu\text{s}$.

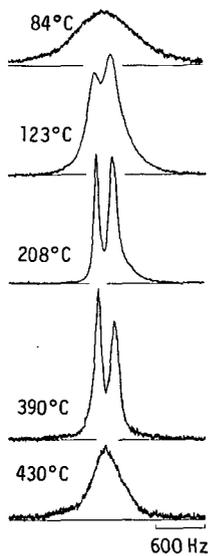


Fig. 6 Proton NMR spectra of ethylene tar pitch at high temperatures.

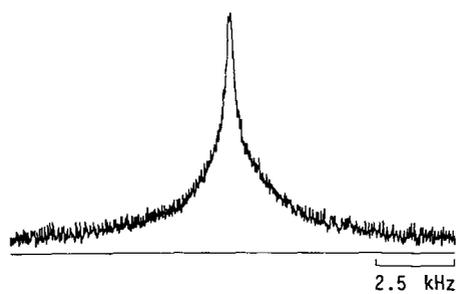


Fig. 7 A proton NMR spectrum of ethylene tar pitch at 470°C.