J. Braz. Chem. Soc., Vol. 18, No. 2, 255-258, 2007.
Printed in Brazil - ©2007 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Communication

Mesophase Formation Investigation in Pitches by NMR Relaxometry

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Piches são utilizados como precursores de diversos materiais avançados de carbono. O objetivo deste trabalho foi combinar as metodologias de extração com solvente com a ressonância magnética nuclear de baixo campo, através da técnica de relaxação, caracterizando piches de petróleo tratados termicamente. O tempo de relaxação T_1 apresentou dois domínios: um na região aromática e o outro atribuído a mesofase. Os resultados mostraram que a técnica de relaxometria por RMN de ^{1}H pode ser empregada como uma nova ferramenta para a caracterização desse tipo de sistema.

Carbonaceous pitches are used as raw materials in advanced carbon products. This work aims at combining solvent extraction methodology with low field nuclear magnetic resonance relaxometry technique in order to characterize heated-treated samples of petroleum pitches. The T_1 relaxation times showed two distinct domains: one was referring to the aromatic region and the other one was attributed to mesophase. The results also evidenced that the ^{1}H NMR relaxometry could be used as a new tool for the characterization of this kind of system.

Keywords: mesophase pitch, nuclear magnetic resonance, low field NMR, relaxometry

Introduction

Carbonaceous pitches are used as raw materials in advanced carbon products.[1] The growth of the mesophase affects the physical properties of the pitch, softening point and viscosity, and also affects the final properties of the resultant carbon products. Several studies were concentrated on the importance of the development of mesophase during the heat treatment of pitches.[2-5] The extensive characterization studies about coal tar and petroleum pitches using liquid and gas chromatography, X-ray diffraction, ^{13}C and ^{1}H NMR, mass spectrometry, optical and electronic microscopy and solvent-insoluble fractions have been summarized by several review articles and books.[2-7] Polarized optical microscopy (POM) and solvent-insoluble fractions are conventional tools for the study and measurement of the amount of mesophase formation.[2,6,8] Although POM is a standard identification tool, extensively used by liquid crystal researchers, Li *et al.*[9] have concluded that conventional POM observation could not be regarded as a good method to analyze the size and size distribution of the mesophase spheres in the isotropic matrix of heat-treated pitches, because of their random distribution. Even the statistical assumptions used in some works could not help to obtain the precise size, since the different apparent sizes could be caused by the random positions. In these random positions spheres were cut in the preparation of the samples and also caused by the size distribution of mesophase spheres in the pitches.

Another analytical method frequently used to follow the growth of the mesophase is solvent extraction. The literature reports a wide range of solvents, e.g. heptane, toluene, tetrahydrofuran, pyridine, quinoline and *N*-methyl pyrrolidinone. However, in different systems, each different extracted material and its extract behave differently. The mesophase spheres in the heat-treated coal tar or petroleum pitches are extracted at a very low yield. Besides, extraction and filtration are very tedious procedures.[2,3,5]

The aim of this work is to combine solvent extraction methodology by using quinoline, *N*-methyl pyrrolidinone and toluene, with low field nuclear magnetic resonance relaxometry technique in order to characterize heated-treated samples of petroleum pitches. Longitudinal proton

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relaxation time data, which is conventionally characterized by relaxation time T_1, was used to investigate the presence of domains in the samples studied. Spin-lattice relaxation reports the return of magnetization to its equilibrium populations after a radio frequency pulse.[3,10-13] Torregrosa-Rodriguez *et al.*[14] and Evdokimov *et al.*[15] have also studied the formation of asphaltene dispersions in oil/toluene solutions by low field NMR relaxation, with measurement of the spin-spin relaxation times (T_2), identifying monomers below 10 mg L^{-1}. In this investigation, low field NMR relaxometry and insoluble fractions techniques were used to characterize different domains in the samples studied.

Experimental

The pitch precursor (sample A) comes from petroleum cracking residue submitted to heating treatment; it was heated at 430 °C *per* 4 hours in a N_2 atmosphere, and five different samples were obtained (samples B-E) as specified in Table 1. Two other pitch samples were obtained from the precursor by density difference with hot stage centrifugation, the upper (isotropic-sample F) and lower (anisotropic-sample G).[16]

The low-field ^{1}H NMR relaxation measurements were done on a Resonance Instruments Maran Ultra 23 NMR analyzer, operating at 23.4 MHz (for protons) and equipped with an 18 mm variable temperature probe operating at 300 K. Proton spin-lattice relaxation times (T_1H) were measured with the inversion-recovery pulse sequence (D_1- π - τ - π/2 - acq.), using a recycle delay value greater than $5T_1$ (e.g. D_1 of 10 s), and π/2 pulse of 4.5 μs calibrated automatically by the instrument software. The amplitude of the FID was sampled for twenty τ data points, ranging from 0.1 to 5000 ms, with 4 scans each point. The T_1 values and relative intensities were obtained with the aid of the program WINFIT by fitting the exponential data. Distributed exponential fittings as a plot of relaxation amplitude *versus* relaxation time were performed by using the software WINDXP.

Results and Discussion

The T_1H relaxation time data obtained at 300 K for the samples studied are shown in Table 2. The mesophase formation can be followed across the distributed exponential fittings as a plot of relaxation amplitude *versus* relaxation time; this was performed using WINDXP software (Figure 1).

Table 1. Characteristics of samples studied

Sample	Insoluble Fraction/(%)		
	Toluene(TI)	Quinoline(QI)	*N*-methyl pyrrolidinone(NMPI)
A	8.8	0.1	0.9
B	24.9	3.8	8.7
C	28.0	7.0	13.5
D	37.1	16.2	24.1
E	57.1	45.1	49.8

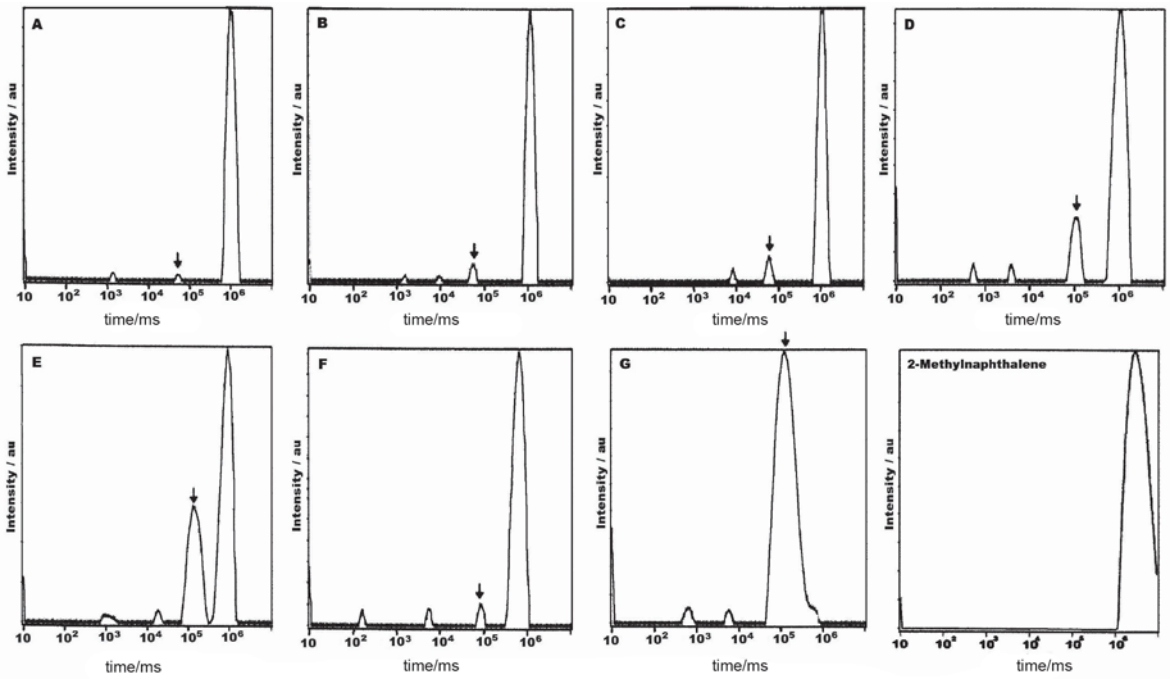

Figure 1. Relaxation amplitude *versus* spin-lattice relaxation times (D_1=10 s, 300 K) of the samples (↓ mesophase domain).

Table 2. Proton spin-lattice relaxation times of the samples determined by low field NMR using WINFIT software

Samples	T_1H^*/(ms)	Intensity	Type of domain proposed	Mesophase/(%)
A	52	8.69	mesophase	2.1
	1012	197.84	aromatic	
	1105	207.68	aromatic	
B	430	107.69	mesophase	26.6
	1322	128.42	aromatic	
	1957	127.33	aromatic	
C	417	20.61	mesophase	52.3
	881	147.66	mesophase	
	808	153.50	aromatic	
D	61	61.70	mesophase	56.9
	746	181.46	mesophase	
	1215	184.46	aromatic	
E	103	110.84	mesophase	64.1
	531	141.21	mesophase	
	1303	141.13	aromatic	
F	0.3	11.12	—	5.4
	60	26.55	mesophase	
	643	452.36	aromatic	
G	11	13.62	—	94.7
	94	127.06	mesophase	
	212	116.73	mesophase	
2-Methylnaphthalene	1521	96.19	aromatic	—
	1745	95.46	aromatic	
	1750	93.77	aromatic	

* These values result from T_1 curve adjustment for three exponentials.

In our studies of T_1 relaxation times, two distinct domains were observed: one referring to the aromatic region and the other was attributed to mesophase. Jurkiewicz *et al.*[10] have used spin-lattice characteristics of coal ^{1}H NMR signals and have suggested that two phases, one molecular and other macromolecular, could be distinguished in the coal structure.

In the present work, T_1H longitudinal relaxation time and the insoluble fraction data were correlated to the presence of different domains in the samples studied (Figure 2). In Figure 2, the highest one belongs to the domain controling the relaxation process, which is a rigid one. The results from the insoluble fraction determinations were lower than those obtained with ^{1}H NMR relaxometry[10] and proved that the mesophase formation was understimated, probably due to the scale of the measurement. It was also observed a good correlation between lower insoluble fraction concentration and NMR relaxation data.

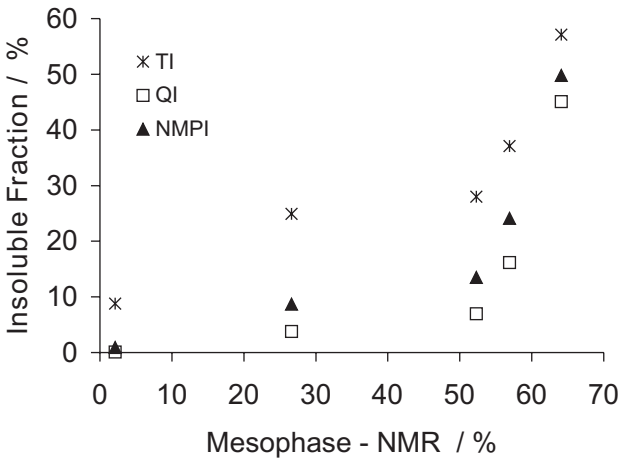

Figure 2. T_1H longitudinal relaxation time data and insoluble fraction of the samples

Conclusions

The NMR relaxation results showed that the system in investigation presented more than one domain, according to their molecular mobility, as a function of phase interaction and dispersion. These results also supported that NMR relaxometry could be used as a new tool for the characterization of this kind of system.

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Received: January 9, 2007
Web Release Date: April 11, 2007