EPR/ENDOR of Separated Fractions of Mesophase Pitches

L. S. Singer, I. C. Lewis, and D. M. Riffle
Union Carbide Corporation, Electrode Systems Division,
Parma Technical Center, 12900 Snow Road, Parma, Ohio 44130, U.S.A.

Introduction

We have recently reported preliminary measurements of the electron paramagnetic resonance (EPR) of the isotropic and anisotropic phases of mesophase pitches separated by high-temperature centrifugation.[1] In this paper, the results of more detailed EPR measurements of saturation, linewidth, and spin concentration are described for the various pitch fractions. Also, electron-nuclear double resonance (ENDOR) and its temperature dependence have been measured. The EPR and ENDOR results can be understood in terms of free radical structure, molecular weight distribution, and molecular mobility in the various phases.

Experimental

The three mesophase pitches employed were derived from naphthalene, petroleum, and QI-free coal tar by standard heat-treatment procedures.[1] The mesophase contents and solubilities are described in Table 1. The mesophase contents were obtained on the centrifuged samples by microscopy techniques described elsewhere.[2] The solubilities of the pitches in pyridine were determined by Soxhlet extraction and the percent pyridine insolubles (PI) are given in Table 1. Other constitutional parameters of the separated phases have already been reported.[1]

The EPR/ENDOR measurements were made with an IBM Instruments, Inc., Model ER/200D-SRC EPR Spectrometer equipped with a low power (90 db) bridge, low and standard frequency signal channels, field-frequency lock, variable temperature system and the ER251 ENDOR/TRIPLE system with the ASPECT 2000 computer.

Table 1. Mesophase Contents and Solubilities of Mesophase Pitches

Mesophase Pitch	Total Mesophase (Vol. %)	Total Isotropic Phase (Vol. %)	PI (Wt.%)
Petroleum	74.7	25.3	54.6
Coal Tar	52.4	47.6	50.0
Naphthalene	39.3	60.7	42.4

The EPR samples were all measured in evacuated or nitrogen-filled sample tubes to eliminate the effects of paramagnetic oxygen. Spin concentrations were obtained by double integration employing small single crystals of $CuSO_4 \cdot 5H_2O$ as primary standards. Because of the long relaxation times of the free radicals in these pitches, all spin concentrations were determined at microwave power levels of 25 μwatts or less.

Results and Discussion

The free radical or spin concentration varies as shown in Figure 1. As expected, for a given pitch, the spin concentration increases with increasing molecular weight of the fraction. The coal tar-derived pitch contains considerably more radicals than the other two pitches, presumably due to its greater aromatic character. The EPR linewidth in Figure 2, except for the pyridine solubles (PS), decreases as a function of molecular weight, as expected. The apparent narrower linewidths of the PS fractions could be the result of the changes in lineshape from predominantly Gaussian to predominantly Lorentzian as the spin concentrations and corresponding molecular weights increase.

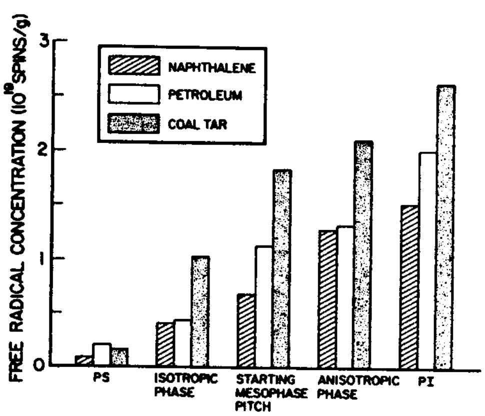

Figure 1. Free Radical Concentration for Various Fractions of Mesophase Pitches Derived from Naphthalene, Petroleum, and QI-Free Coal Tar.

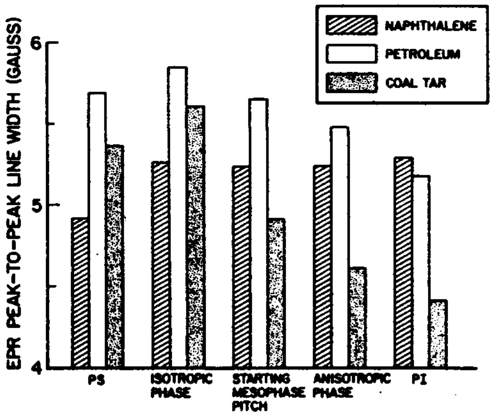

Figure 2. EPR Peak-to-Peak Linewidths for the Mesophase Pitches and Fractions Described in Figure 1.

The saturation behavior indicates the dramatic dependence of the electron spin-lattice relaxation time, T_1, on radical concentration and molecular size. Figure 3 shows Blombergen-Purcell-Pound (BPP) saturation plots[3] for the different fractions of the naphthalene-derived mesophase pitch. The microwave power, $P_{1/2}$, at which the normalized EPR amplitude falls to one-half of its unsaturated value, is a convenient quantitative parameter which correlates with the inverse of the spin-lattice relaxation time T_1. These curves emphasize the low powers required for meaningful EPR measurements of spin concentrations and lineshapes. Different types of saturation plots, such as suggested by Portis,[4] prove that the pitch free radicals, even in a separated fraction, cannot be described by a single relaxation parameter, but must be described by a distribution of relaxation times, as the molecular weight distribution would suggest.

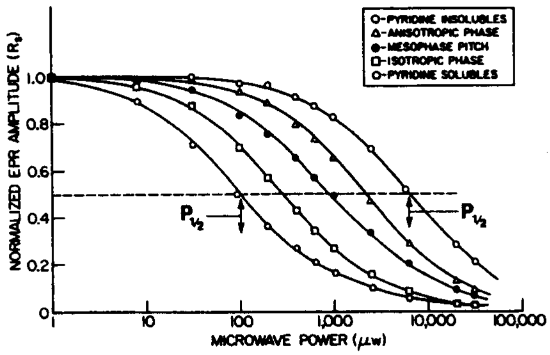

Figure 3. EPR Saturation Curves for the Various Fractions of the Naphthalene Mesophase Pitch. The parameter $P_{1/2}$ is defined as the microwave power at which the normalized EPR amplitude falls to one-half of its unsaturated value.

The ENDOR phenomenon in pitches[5,6] indicates two interactions between electron spins and the many protons present, namely a hyperfine ENDOR due mainly to Fermi contact interactions, and a matrix or distant ENDOR at the free proton frequency due to anisotropic electron-nuclear dipolar interactions. The latter depends very sensitively on molecular motions and thus temperature as shown in Figure 4 for the isotropic and anisotropic phases of a petroleum mesophase pitch. The precipitous drop in matrix ENDOR intensity occurs in the vicinity of the glass transition temperature of these and other pitch materials.

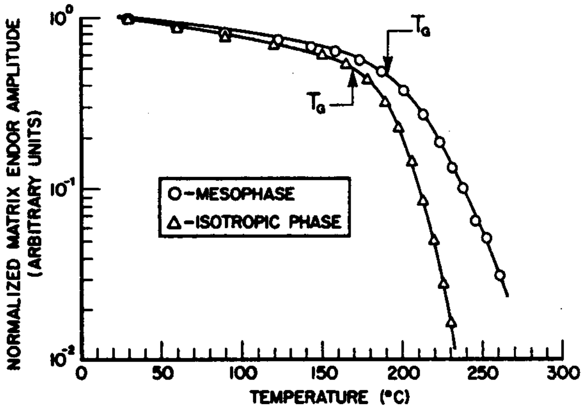

Figure 4. Matrix ENDOR Amplitude as a Function of Temperature for the Isotropic and Anisotropic Phases of a Petroleum Mesophase Pitch. The amplitudes were normalized to unity at 30°C. The DSC glass transition temperatures are denoted by T_G.

References

1. L. S. Singer, I. C. Lewis, and R. A. Greinke, "Carbone 84," International Carbon Conference, Bordeaux, France, July 2-6, 1984, Extended Abstracts, pp. 352-353.

2. L. S. Singer and D. M. Riffle, to be published in CARBON.

3. N. Bloembergen, E. M. Purcell and R. V. Pound, Phys. Rev. 73, 679 (1948).

4. A. M. Portis, Phys. Rev. 91, 1071 (1953).

5. L. S. Singer and I. C. Lewis, Extended Abstracts, 16th Biennial Conference on Carbon, San Diego, California, July 18-22, 1983, pp. 429-430.

6. L. S. Singer and I. C. Lewis, CARBON (in press).