7026 *Macromolecules* **1995,** *28,* 7026−7028

Communications to the Editor

Superconducting Quantum Interference Device Magnetic Susceptibility Measurements: Determination of Free-Radical Concentrations in PMR-15 Polyimide Resin

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Received March 14, 1995
Revised Manuscript Received July 28, 1995

A reliable determination of free-radical concentrations is desirable in understanding polymer stability. In this communication we report establishing an absolute free-radical concentration by measuring the magnetic susceptibility of a PMR-15 sample using a superconducting quantum interference device magnetometer (SQUID). This concentration value may be used as a reference point in determining free-radical concentrations of polyimides and other polymers by their electron paramagnetic resonance (EPR or ESR) spectral intensity comparisons.

PMR-15 polyimide is a high-performance polymer that is widely used in high-temperature applications of composites.[1,2] Free radicals are generated when the resin samples are exposed to temperatures above 573 K and are found to be relatively stable at room temperature. The presence of these free radicals at room temperature in this polyimide has been confirmed recently by EPR spectroscopy of PMR-15 resin samples.[3,4] The weight loss data at elevated temperatures suggest that these free radicals are directly involved in the oxidative degradation of the polyimide in the presence of oxygen.[3]

Although the EPR technique is a very sensitive way of detecting free radicals in a sample, establishing an absolute concentration of the free radicals by EPR is rather difficult because of the following: (i) The EPR method requires calibration against spin concentration standards, which are often unreliable. (ii) For a complex spectrum, the spin concentration is determined by a double integration of the experimental signal. For a spectrum with broad wings, this procedure can be inaccurate depending on the spectral window chosen. (iii) Dielectric samples may affect the intensity of the EPR signal because the microwave power loss in a dielectric material alters the distribution of the microwave field in the resonator. For these reasons, we have measured the static magnetic susceptibility of a PMR-15 resin sample using a SQUID magnetometer. The concentration of free radicals in this sample is established absolutely from the measured susceptibility.

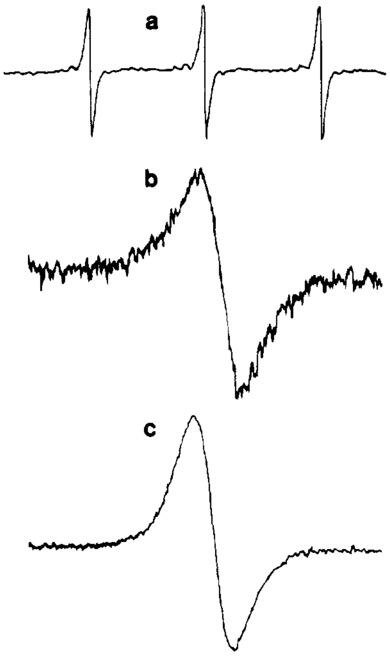

Figure 1. Room temperature first-derivative X-band EPR spectra of (a) reference samples consisting of di-*tert*-butyl nitroxide in benzene (the location of the center peak corresponds to a *g*-value of 2.0063, and the outer peaks are separated by 30.36 G); (b) the cured PMR-15 resin sample aged in air for 16 h at 589 K; (c) the same sample further aged in an atmosphere of nitrogen for 30 h at 644 K. This additional aging at the higher temperature results in a better signal-to-noise ratio corresponding to a higher concentration of free radicals. Note that 1 G equals 0.1 mT.

The SQUID technique is also very sensitive. In principle, the minimum detectable susceptibility is $\chi = 10^{-15}$ emu/g in a 10 T magnetic field, while typical sensitivity is about 10^{-13} emu/g.[5] A magnetic moment measured in a SQUID experiment includes the combined effects of paramagnetism and diamagnetism. The temperature dependence of the susceptibility can be characterized by the Curie−Weiss law in order to separate para- and diamagnetic effects and to derive free-radical concentrations.[6,7]

Experimental Section. A PMR-15 polyimide resin sample was provided to us by Dr. Kenneth Bowls and his colleagues at NASA Lewis Research Center. It was prepared following a standard method[8,9] and was subjected to aging for 16 h in air at 589 K. Portions of this sample, designated II63-3, were used for EPR and SQUID experiments. The X-band (9.5 GHz) EPR spectrum shown in Figure 1 was obtained with a Varian V-4502 EPR spectrometer. The room temperature spectrum exhibited a single line at a *g*-value of 2.0039[10] with a derivative peak-to-peak width of 0.57 mT.

Measurements of total magnetization, *M*, of the sample were carried out with the MPMS (Quantum Design, CA) SQUID magnetometer system following experimental procedures previously described.[6] For the susceptibility measurements, oxygen molecules adsorbed in the sample were eliminated by repeatedly

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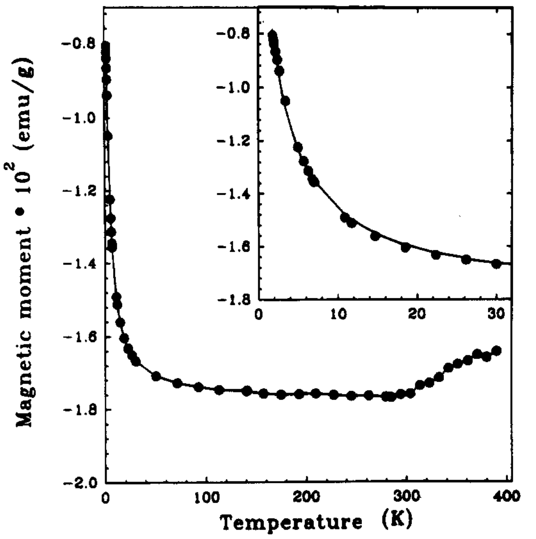


Figure 2. Temperature dependence of magnetic susceptibility of the cured PMR-15 polyimide resin aged in air. The measurements were carried out with the SQUID magnetometer at a fixed static magnetic field of 10 kG. Each experimental point is an average of three scans with a standard deviation of no more than 0.2%. The insert shows the expansion of the temperature region 1.8–30 K. The solid line is the best fit with Curie–Weiss law. Other features in the higher temperature regions are discussed in the text.

pumping and purging the sample chamber with helium gas for 1.5 h before the measurements were recorded. Incomplete elimination of the adsorbed oxygen would produce additional magnetic susceptibility variations due to paramagnetic to antiferromagnetic oxygen transitions at 57 K.[11] The antiferromagnetic phase of oxygen should not contribute significantly to the total paramagnetic susceptibility below this transition temperature. However, the presence of molecular oxygen in a sample would interfere with SQUID data analyses above the transition temperature, making the SQUID determination of unpaired spin density less reliable. The experimental data discussed below showed no evidence of residual oxygen.

Results and Discussion. The temperature dependence of the static susceptibility, shown in Figure 2, was measured at a fixed static magnetic field, H, of 1 T over the temperature range of 1.8–400 K. In the temperature region of 1.8–280 K, the magnetization decreases because of the diminishing paramagnetic contribution of the free radicals in the sample. In the temperature region of 280–400 K, the magnetization gradually increases. In the SQUID data analyses, we have excluded paramagnetic ion impurities from consideration, since no EPR signals which may be attributed to these ions have been observed for oligomer or cured polyimide resins.

The negative value of the susceptibility throughout the entire temperature range indicates that the paramagnetic contribution to the total susceptibility is small compared to the diamagnetic contribution. The negative values for M and the negative slope of the M vs H plot in Figure 3 also demonstrate that the static susceptibility, χ, given by $M = \chi H$, is largely diamagnetic at the temperature of 4.5 K, where the paramagnetic contribution is expected to be considerably larger than at a higher temperature.

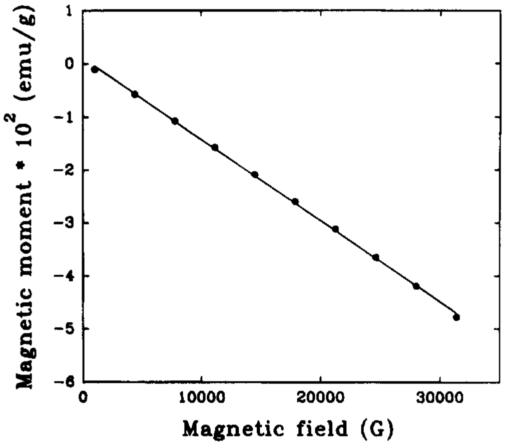


Figure 3. Total magnetization at 4.5 K for the cured PMR-15 polyimide resin aged in air as a function of the applied magnetic field strengths, H, in gauss. The negative slope shows that the diamagnetic contribution dominates.

The magnetic susceptibility in the low-temperature region follows the Curie–Weiss law, given by[12]

$$\chi = \{P/(T + \theta)\} + \chi_0 \tag{1}$$

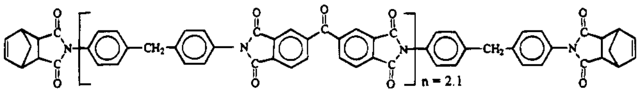
with

$$P = Ng^2\mu_B{}^2S(S + 1)/3k_B \tag{2}$$

where T is the absolute temperature, Θ is the Weiss constant, N is the number density of the unpaired electrons, μ_B is the Bohr magnetron, the spin quantum number, S, is $^1/_2$ for a doublet-state unpaired electron, and k_B is the Boltzmann constant. The temperature-independent term, χ_0, includes the diamagnetic susceptibility[13] and the Pauli paramagnetism of any free charge carriers which may be present in the sample.[14]

The best nonlinear least squares fit of the experimental data in the temperature range of 1.8–157 K to the Curie–Weiss law is shown as a solid line in Figure 2 and the insert of Figure 2. The best-fit parameters are $P = 4.01 \times 10^{-6}$ emu K/g, $\Theta = 2.2$ K, and $\chi_0 = -1.79 \times 10^{-6}$ emu K/g. Note that the positive Weiss constant suggests the possibility of a small contribution from antiferromagnetic spin exchange processes of unpaired electrons.[6] Using eq 2 with this value of P and assuming the spin quantum number $S = {}^1/_2$ with $g = 2.00$, we obtain the free-radical concentration, N, of 6.3×10^{18} free radicals per gram of sample. In the following discussion, we refer to this value of N as the SQUID-measured free-radical concentration (SQFRC) value.

The PMR-15 is initially prepared in the oligomeric form with a formula molecular mass of 1500.[8] Therefore, this SQFRC corresponds to an average of 1.6 free radicals in each of the 100 PMR-15 oligomer units. The structure of oligomer unit is shown below:



Note that PMR-15 is prepared by thermally cross-linking the norbornene endcaps of this oligomer at temperatures above 525 K.[9] In many of the PMR-15 samples that were aged under a controlled atmosphere at elevated temperatures of 623 and 643 K, we have reported[3,4] X-band EPR spectral intensities that were 2–3 orders of magnitude larger than that in the sample used for this SQUID measurement. The SQFRC value may be used as an absolute reference in determining free-radical concentrations of polyimide samples by comparing EPR intensities. This determination is possible because the integrated EPR intensities are proportional to the number of free radicals present in the sample. Such comparisons are simpler and more reliable when the EPR spectral line shapes and line widths are the same and their dielectric properties are similar for all the samples to be compared. In such cases the free-radical concentrations are directly proportional to the peak-to-peak first-derivative height. For example, the sample whose X-band EPR spectrum is shown in Figure 1c has been aged for 16 h in air at 589 K and then aged further for 30 h in nitrogen gas at 644 K. If we assume that the spectrum in Figure 1b is produced by the free-radical concentration determined by SQFRC, the comparison of the intensities of spectra b and c in Figure 1 gives a free-radical concentration of 30 unpaired electrons in each of the 100 oligomer units for this sample.

The magnetic susceptibility in the temperature region of 280−390 K increases from approximately −0.018 to −0.016 emu/g. Since the total susceptibility is negative, one possible explanation of this increase is the loss of diamagnetic material as the sample is heated in this region. The anomalous behavior of the EPR intensity reported earlier[4] for this temperature range rules out this possibility. The EPR intensity also increases as a PMR-15 sample is heated above 230 K. It reaches a maximum near 353 K and decreases rapidly above 393 K. This anomaly in temperature-dependent EPR intensity is interpreted[3,4] as an indication that another free-radical species, different from the one responsible for the paramagnetic susceptibility in the lower temperature region, is being generated as the temperature is increased. The presence of two distinct free-radical species in PMR-15 and other polyimide samples has been confirmed by the 1 mm frequency band (250 GHz) EPR spectra.[15] Note that the SQFRC value, which is estimated at the low-temperature region, does not include any contribution from this new type of free radical generated in the higher temperature region.

Acknowledgment. M.K.A. thanks Dr. Mary Ann B. Meador, Dr. Michael A. Meador, and their colleagues of the Polymers Branch of the NASA Lewis Research Center Materials Division for providing polyimide samples and other support. Thanks are also due to Professor John Allen for his comments. This research used facilities of the Illinois EPR Research Center, an NIH BRTP Research Resourse (NIH P41-RR01811).

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MA9503367