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NOTES

Kinetics of crystallization in conducting polymers observed from electron spin resonance

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The possibility of doping conjugated polymers with donors or acceptors species, made available a new class of materials, the conducting polymers. These materials not only have their conductivity increased by several orders of magnitude but also exhibit a broad variety of spin behavior with the observation of Pauli susceptibility, polarons, solitons or spinless bipolarons.^{1,2} In previous works^{3,4} we have observed cooling rate dependent electron spin resonance (ESR) data in pressed pellets of ClO_4^- and BF_4^- doped P3MT. A single ESR line became distorted around 240 K and was changed into a broad and a narrow superimposed lines below 225 K. The amount of the broad line contribution was dependent on the cooling rate, decreasing with increasing cooling rate. Above 240 K no cooling rate effects were observed. From the change in the electronic and spin behavior in the range 220 K–240 K we have explained our ESR data in terms of metal–insulator transitions. In this work we show new ESR experiments performed in samples that were supercooled from room temperature to 110 K and rapidly brought to the temperature of 223 K. The evolution of the ESR spectrum with time made it possible to understand the cooling rate dependent data in terms of crystallization and follow its kinetics.

Pressed pellets of ClO_4^- doped poly(3-methylthiophene) were electrochemically synthesized as described in Ref. 3. X-band ESR measurements were performed in a Varian E-109 reflection spectrometer using a TE_{102} rectangular cavity adapted to a cold nitrogen gas flow system. Figure 1 shows the ESR spectra at different times for sample A (thickness $d=80\ \mu\text{m}$) obtained after quenching the sample to 110 K

and suddenly raising the temperature to 223 K. Although it seems that the width of the ESR line is changing with time, the spectra is composed of two superimposed lines,³ with different widths, whose amplitudes have a significant change with time for approximately 1 h. No change with time is observed at this temperature, when the sample is slowly cooled from room temperature. The ESR spectra were fitted assuming two Lorentzian absorption lines with different widths and amplitudes. Although the linewidths remain the same, the amplitudes change with time. For the narrow line we have found $\Delta H_{1/2}=7.65\ \text{G}$ and for the broad line $\Delta H_{1/2}=23.85\ \text{G}$.

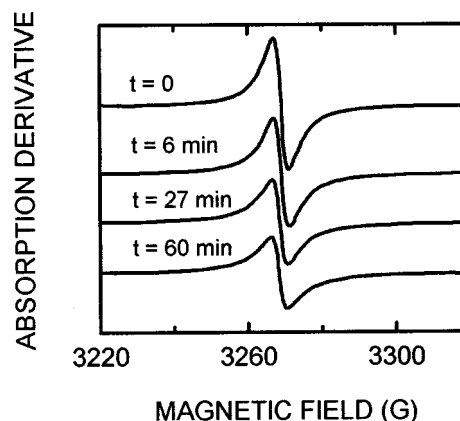


FIG. 1. ESR spectra at 223 K (absorption derivative in arbitrary units) is shown at four different times for sample A, quenched from room temperature to 110 K and rapidly heated to 223 K.

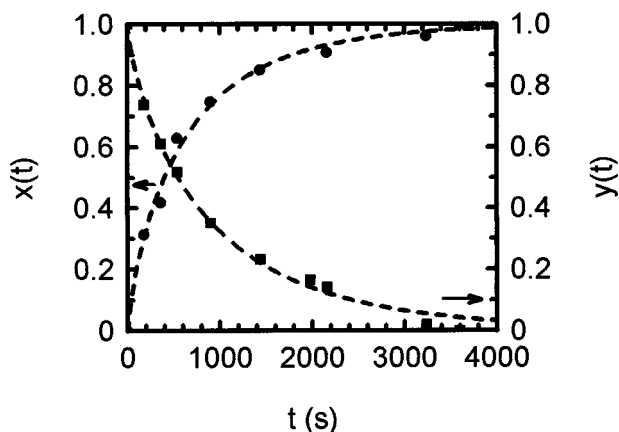


FIG. 2. (Circles) Fraction of crystallization $x(t)$ vs time for sample A. (Dashed line) Fit using Avrami's equation, $x(t) = 1 - \exp(-Kt^n)$ for $K = 0.0057$ and $n = 0.801$. (Squares) Fraction of decrease of the amorphous phase $y(t)$ vs time. (Dashed line) Fit to $y(t) = \exp(-Kt^n)$, for $K = 0.0043$ and $n = 0.806$.

In Fig. 2 we plot the data obtained from the fit of the ESR spectra of sample A, for the broad line (circles). We plot $[A_B(t) - A_B(0)]/[A_B(t_M) - A_B(0)]$ vs t , where $A_B(t)$ is the broad line amplitude at time t , $A_B(0)$ is the same for $t = 0$ and $A_B(t_M)$ is the broad line amplitude for the last spectrum that we observed to vary with time. The data plotted in this way has the advantage to be zero at $t = 0$ and one at $t = t_M$. In this sense they can be identified with the fraction of crystallinity $x(t)$ for an isothermal crystallization, and can be adjusted by Avrami's equation⁵⁻⁷

$$x(t) = 1 - \exp(-Kt^n), \quad (1)$$

where K is a constant for a fixed temperature and n depends on the system's dimensionality. The dashed line is the fit with $K = 0.0057$ and $n = 0.801$. We also plot the data for the narrow line (squares). We plot $y(t) = [A_N(t) - A_N(t_M)]/[A_N(0) - A_N(t_M)]$ vs t , where $A_N(t)$, $A_N(t_M)$, and $A_N(0)$ are the narrow line amplitudes at time t , $t = t_M$, and $t = 0$, respectively. The dashed line is the fit for the narrow line data assuming

$$y(t) = \exp(-Kt^n), \quad (2)$$

yielding $K = 0.0043$ and $n = 0.806$.

In Fig. 3 we show the differential scanning calorimetry (DSC) data of sample B (mass = 7.1 mg) after being quenched from room temperature at a rate of 20 K/min. The drop of the temperature was sufficiently fast to supercool the sample, because an exothermic peak was observed in the range 220 K–240 K when the temperature was raised at a rate of 10 K/min. An exothermic peak was also observed in the same range, when the sample was cooled from room temperature at a rate of 10 K/min. We can unambiguously associate this range of temperature as the one in which crystallization takes place into the polymer. The experiment was performed in a Netzsch Thermal Analysis DSC 200 using a PASC 414/3 temperature controller.

The Avrami exponent obtained from the fit of the broad

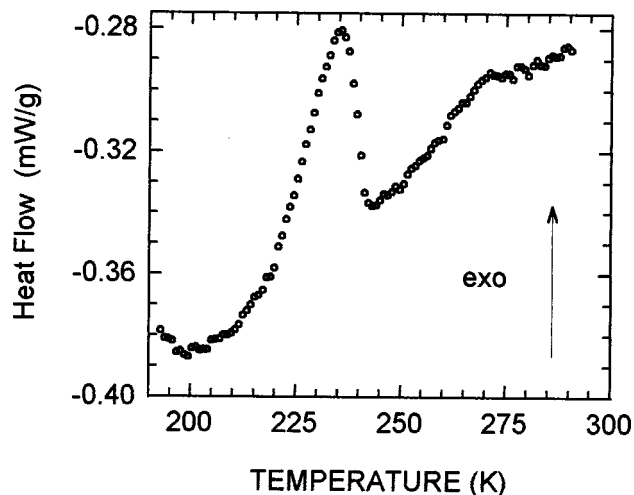


FIG. 3. DSC curve of sample B. After cooling the sample to 110 K at a rate of 20 K/min, the data were collected raising the temperature to room temperature at a rate of 10 K/min.

line in Fig. 2 can be understood assuming one-dimensional crystallization with the formation of an anisotropic structure.⁸ This result is not surprising because not only the chain direction in conjugated polymers is a preferential direction, but also the pressure used to make the pellets reinforces it. We can observe that the fit parameters in Fig. 2 are very close. This is indicating that the amorphous phase is disappearing at the same rate as the crystalline phase is increasing.

To know the behavior of the total number of spins, we added the intensity of both lines and observed a net decrease of 10% in the total number of spins in the whole time interval. This decrease suggests that some spinless bipolarons have been created in the ordering process.

In summary, we have shown that in conducting polymers, kinetics of crystallization of a supercooled sample can be studied using ESR. This technique can also give information about the cooling rate amount of crystallization, by measuring the increase of the broad line contribution in experiments performed with different cooling rates.⁴ The advantage of using ESR is its simplicity. More sophisticated data on the kinetics of crystallization in polymers has been obtained using Synchrotron Radiation Small Angle Scattering.⁹

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