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An Anomalous Voltage Effect Observed During Melting and Crystallization of Poly(ethylene Oxide)

Some unexpected results were obtained with poly(ethylene oxide) in attempts to measure a pyroelectric effect on thin films. These are described below.

EXPERIMENTAL

A Leitz dialux-pol polarized light microscope fitted with a thermostated hot stage controlled to 0.2°K with an electronic temperature controller (Eurotherm) was used to examine thin films during measurement. A thermocouple amplifier, Comark Model 1604, was used to measure the temperature of the sample to 0.1°K.

A precision nanovolt dc amplifier, Keightley Instruments Ltd. Model 140, was used to determine voltage differences across the samples. The voltage difference was displayed on a single-channel chart recorder, Bryans Southern Instruments Model 2800, fitted with an input filter to reduce the noise level.

Thin polymer sheet, 0.01–0.1 mm thick, was prepared by compression molding. Specimens $1 \times 1 \text{ cm}^2$ were cut from this sheet and mounted between two annular ring copper electrodes. This was placed between glass cover slips and secured in the hot stage of the microscope. Thin wire electrical leads were soldered directly on to the electrodes, sheathed, and connected to the dc amplifier with the special thermal plug designed to eliminate spurious metal contact potentials. The correct input impedance was obtained by shunting the electrodes with a 30-kohm resistance. Voltage differences of 1 nV could be detected by this apparatus.

A Union Carbide poly-ox resin WSR 205 was used in this study, but other poly(ethylene oxide) samples exhibited the same effects.

RESULTS AND DISCUSSION

A number of polymers were investigated with a view to detecting possible pyroelectric and/or piezoelectric effects. No piezoelectric effect was detected in any polymer studied over the pressure range used (i.e., within the quasi-elastic range in each case). In the case of poly(ethylene oxide), however, a voltage difference was observed on heating thin films between two similar metal electrodes, but this did not change substantially with increasing temperature until in the temperature range in which the polymer was observed to melt. A marked increase in voltage was then observed (see Fig. 1), and subsequent heating of the polymer melt did not produce any further significant voltage changes. The voltage change appeared to be associated with a phase change rather than a pyroelectric effect, since a reversal of the voltage change was observed on recrystallization on cooling. The appearance or disappearance of the spherulites and birefringence in the sample between the electrodes was used to monitor the onset of the phase change.

PVC, polyethylene, polypropylene, polystyrene, poly(methyl methacrylate), nylon, poly(tetrahydrofuran), and poly(vinylidene fluoride) were examined in an identical fashion to that adopted for examining poly(ethylene oxide), but no reproducible voltage changes were observed. Accordingly, the voltage changes were associated with the phase change in poly(ethylene oxide) rather than the pyroelectric effect, particularly since poly(vinylidene fluoride) gave no similar voltage changes.

The absence of a piezoelectric effect over the stress range studied (i.e., below the stress value associated with the onset of plastic deformation) also suggests that a pyroelectric effect is precluded since a pyroelectric effect is always accompanied by piezoelectric properties.

The voltage change with the poly(ethylene oxide) samples was reproducible from sample to sample, and it increased on melting. Interchanging the leads and also the ring electrodes did not reverse the polarity of the voltage difference nor alter the size of the change on melting. However, altering the metal of the electrode altered the voltage change on melting, see Table I. Very occasionally, the voltage observed was reversed in polarity with a sample, but in general the polarity was the same from sample to sample. There was no effect of light, nor was there any effect from infrared radiation from a low-temperature radiating heat source, such as a soldering iron, as would be the case were the polymer film behaving pyroelectrically.

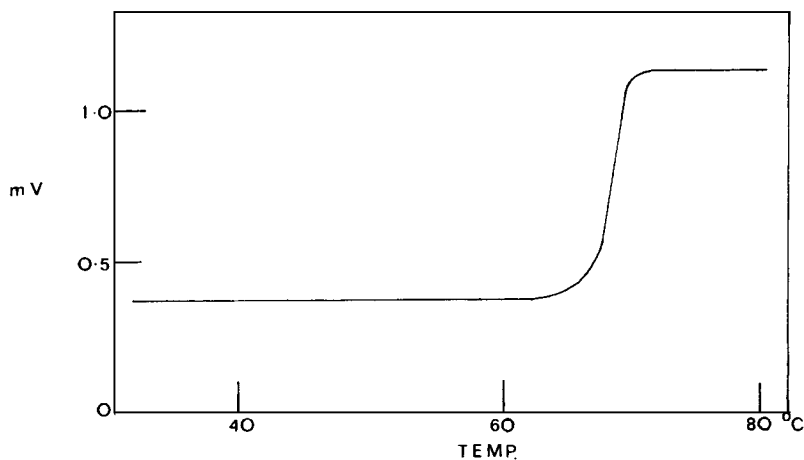


Fig. 1. Temperature dependence of the voltage difference.

TABLE I
Voltage Differences on Melting Poly(ethylene Oxide)

Electrode material	mV
Copper	0.70
Steel	0.17
Aluminum	0.088

Consistent with the changes observed on melting, the progress of the isothermal crystallization of polyethylene oxide could be followed by the progressive change in the voltage difference with time (see Fig. 2). The decrease in voltage was accompanied by the production and growth of spherulites, and if it was assumed that the relative drop in voltage was proportional to the crystallinity developed, the time dependence of the crystallization could be determined for comparison with that measured on the same sample by more conventional techniques, e.g., differential scanning calorimetry (Perkin-Elmer DSC 2).

When a polymer crystallizes from the melt, the extent of crystallization is related to time by the Avrami equation

$$1 - X_t = \exp(-Zt^n) \quad (1)$$

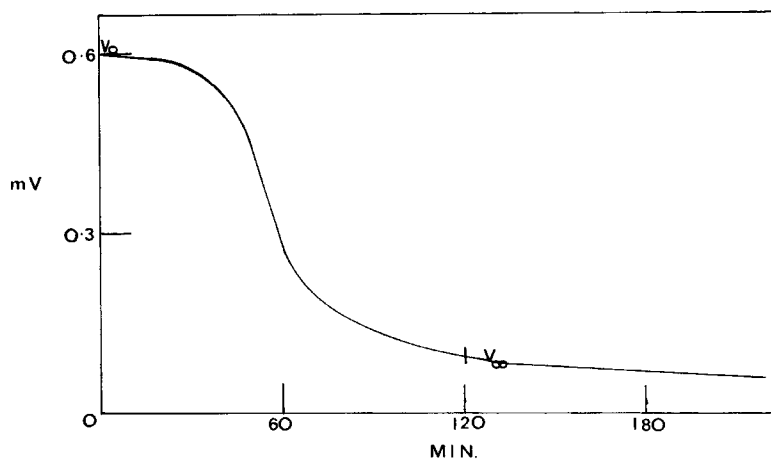


Fig. 2. Voltage change on isothermal recrystallization of poly(ethylene oxide) at 329°K.

TABLE II
 Crystallization Characteristics

Temp, °K	Rate constant Z , min^{-n}	n	Degree of fit (\bar{r}) ²
Voltage Difference			
325.0	9.1×10^{-2}	1.40	0.970
327.0	1.2×10^{-2}	1.78	0.990
329.0	4.2×10^{-4}	1.80	0.940
DSC Measurement			
325.0	8.9×10^{-2}	1.70	0.985
326.0	1.7×10^{-2}	1.75	0.980
327.0	4.5×10^{-3}	1.90	0.997
328.0	8.7×10^{-4}	2.20	0.978

in which Z is a composite rate constant including nucleation and growth rate constants, and n is an integer diagnostic of the crystallization mechanism. The general shape of the relative voltage change-time plots was consistent with a two-stage crystallization,^{1,2} namely, a primary stage following the time dependence of eq. (1) and a secondary one exhibiting a logarithmic time dependence. Accordingly, only the initial portion was analyzed by eq. (1). In this analysis, it was assumed that

$$X_t = (V_0 - V_t)/(V_0 - V_\infty)$$

in which V_0 , V_t , and V_∞ are the measure voltage differences initially, at time t , and finally V_∞ was used as an adjustable parameter to indicate some separation between primary and secondary crystallization. Z and n were determined from a least-squares fit of

$$\log (\ln (V_0 - V_\infty)/(V_0 - V_t)) = \log Z + n \log t \quad (2)$$

These values are listed in Table II along with comparable data obtained from the isothermal crystallization of the same polymer thin film sample measured by DSC. Reasonable agreement was found between the two sets of Z and n values and the degree of fit (\bar{r})² of eq. (2) to the crystallization data to indicate that the voltage change follows closely the changing crystallinity of the polymer.

However, the voltage differences measured on melting and recrystallization are unlikely to be associated with a pyroelectric effect since they are greatest with noncrystalline material. These voltage differences are either associated with a spurious response due to an inhomogeneous distribution of trapped charges within the polymer³ or with an electrochemical cell set up between the electrodes and the amorphous regions of the partially crystalline polymer with some inhomogeneity in the distribution of the electrolyte. It is tempting to attribute the electrolyte to adsorbed water, but most of the experimental evidence is against this assumption. Extensive heating of the melt, in air and in vacuo, had no effect on the size of the voltage change, and the voltage difference is greatest within the melt when concentration inhomogeneities would disappear with time.

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