Electrical conduction in poly(ethylene-2,6-naphthalate) films of varying crystallinity

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Electrical conductivity in poly(ethylene-2,6-naphthalate) (PEN) film was investigated. Electronic conduction was found to exist at temperatures below 333 K and an increase in the crystallinity was found to enhance the photocurrent of PEN. However, a further increase in crystallinity which was followed by the formation of excimer sites caused a decrease in the photocurrent.

INTRODUCTION

Conventional polymer films are, in general, insulators and any electrical conduction has been attributed to ionic impurities included in polymers. However, the development of electroconductive polymers, such as polyacetylene and polypyrrole, has raised interest in electronic conduction in insulating polymers. One of the more important objectives in this area may be the elucidation of the interrelation between higher-order structures and electronic conduction in polymer films. Several papers have dealt with the dependence of the mobility of electronic carriers on the degree of crystallinity in polymer films[1-4]. However, there is considerable divergence of opinions on this matter.

Electronic conduction in poly(ethylene-2,6-naphthalate) (PEN) film is of particular interest, because PEN has a fairly large π-conjugated ring in the main chain. In fact, one can easily observe a photocurrent, which is an indicator of electronic conduction. Furthermore, several authors[5,6] have observed an excimer fluorescence, which indicates the presence of strong interactions between the naphthalene rings; the photo-carrier generation and charge transport in PEN films are expected to be closely related to these strong interactions.

In this paper, we have investigated the dark conduction and photoconduction in PEN films with varying degrees of crystallinity, and the effect of the crystallinity on the electronic conduction in PEN films is discussed.

EXPERIMENTAL

Biaxially oriented poly(ethylene-2,6-naphthalate) (PEN) films (thickness = 100 μm) were kindly supplied by Teijin Ltd., Japan. Their degree of crystallinity was about 45%. The films were melted at 553 K in a compression mould and quenched to 273 K. The amorphous PEN films of 100 μm thickness were then obtained. These films were then annealed at given temperatures for 15 min to obtain crystalline samples. The degrees of crystallinity were evaluated from their densities, which were measured by

the flotation method. The crystal density of 1.407 g cm^{-3} and the amorphous density of 1.325 g cm^{-3} were used[7,8].

Semi-transparent gold electrodes were evaporated onto the samples. Conductivity measurements were made using a vibrating reed electrometer (Takeda Riken, TR-84M). The photocurrent was measured using a 1 kW xenon lamp with a u.v. pass filter (Toshiba UV-D36B) as a light source. Corrected fluorescence spectra were obtained by using a Hitachi 650-60 fluorescence spectrometer.

RESULTS AND DISCUSSION

Electrical conductivity

Figure 1 shows the temperature dependence of the electrical dark conductivity in biaxially oriented PEN film measured in dry air and *in vacuo*. The measurements were performed after annealing the sample at 433 K for 2 h in a dark chamber. No pronounced difference in the dark conductivities in air and *in vacuo* was found, and the log σ vs. T^{-1} relation could be approximated with three straight lines giving two break points, T_g (381 K) and T_b (333 K), as shown in Figure 1. The break point at the higher temperature corresponded to the glass transition temperature of PEN (386 K). This finding implies that the carriers contributed to the electrical conduction are ionic impurities in the temperature region crossing the T_g. This assignment can be supported by the measurement of photoconduction in PEN.

Figure 2 shows the temperature dependence of the photocurrent of the PEN film. The photocurrent is concerned with the transport of electronic carriers, which are produced through the absorption of photons. Both activation energies of dark conduction, which were calculated from the slopes of the log J vs. $1/T$ plots, in the temperature region above T_g and the region between I_g and T_b were much higher than that for the photocurrent. Therefore, the conduction processes in the temperature region above T_b are governed by the carriers (ionic impurities) and influenced by the molecular motion in PEN around the glass transition. However, carrier species below T_b are assumed to be electronic, since the activation energy of dark conduction below T_b is close to that of the
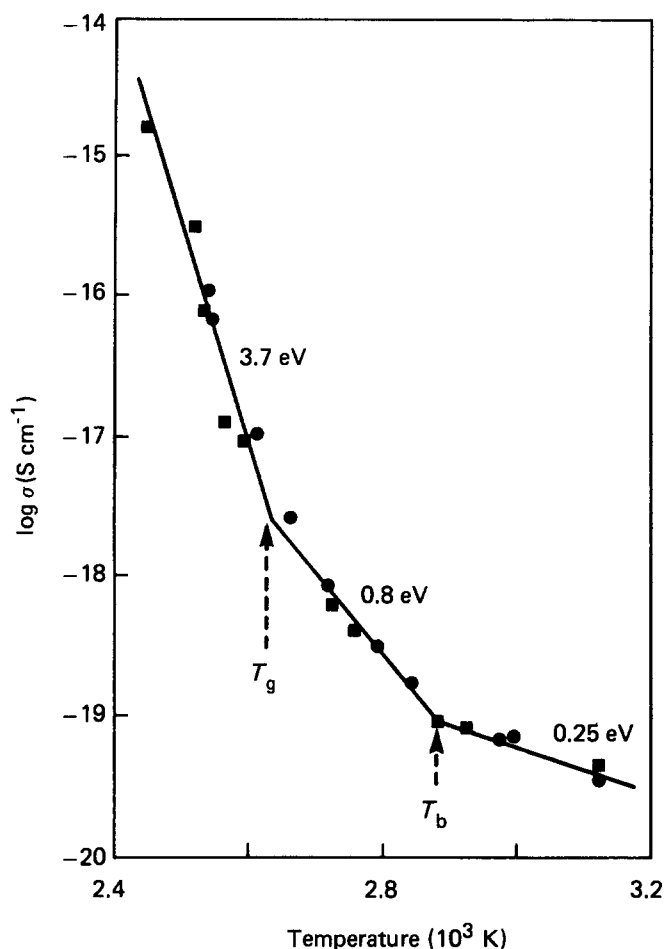
Figure 1 Temperature dependence of dark conductivity in the biaxially oriented PEN film annealed at 433 K: (●) in air, (■) *in vacuo*
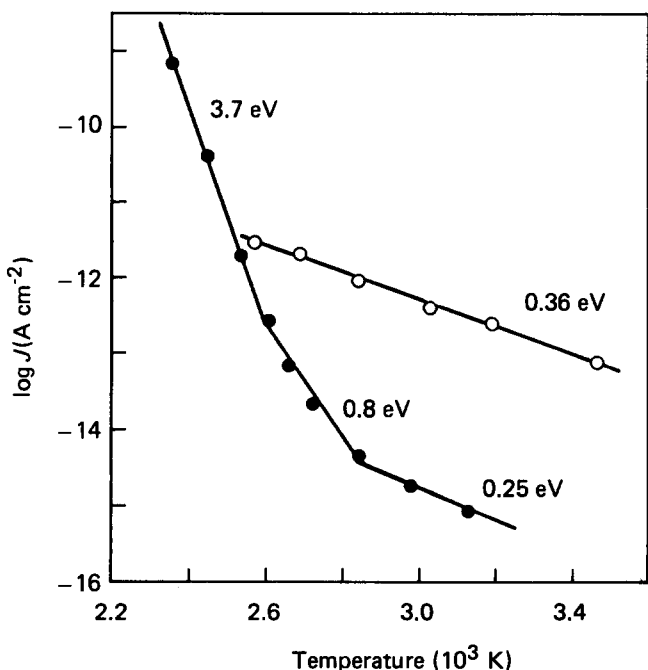

Figure 2 Temperature dependence of photocurrent (○) and dark current (●) in the PEN film. Activation energies in eV are shown

photocurrent. This assumption may also be supported by the following experimental facts.

Figure 3 shows the effect of u.v. irradiation on the temperature dependence of the dark conductivity of the PEN film. Curve A indicates the log σ vs. T^{-1} relation of the as-received PEN film measured with ascending

temperature. Curve B is the plot measured with descending temperature after the sample was annealed at 433 K in dark conditions. After the sample had been irradiated with u.v.-light at room temperature, curve C was obtained. Curve D, which was very close to curve B, was obtained after the u.v.-irradiated sample had been annealed again at 433 K. These differing responses can be ascribed to neither chemical change nor change of aggregated structures of molecules in PEN, because the u.v.-irradiation effects had been observed with repeated measurements. Some variation of the physical states of the film could, however, be postulated. That is to say, the effect of photo-irradiation on the apparent dark conductivity may be concerned with trapped electronic carriers. The u.v.-irradiation produces a large number of electronic carriers, they are captured in deep trap centres in the bulk of the PEN film, and the trapped carriers are gradually released with the aid of applied voltage. Somewhat similar phenomena have been reported with poly(N-vinyl carbazole)[9] and poly(p-phenylene sulphide)[10].

Table 1 summarizes the dark conduction processes in PEN films. We can conclude that electronic conduction exists latently in PEN, which is an electrical insulator, though the contribution to the total electric conduction is rather small.

Effects of crystallinity on electronic conduction

The absolute values of the dark electronic current were extremely small, as shown in *Figure 2*. Photocurrents were employed to evaluate the effect of crystallinity on the
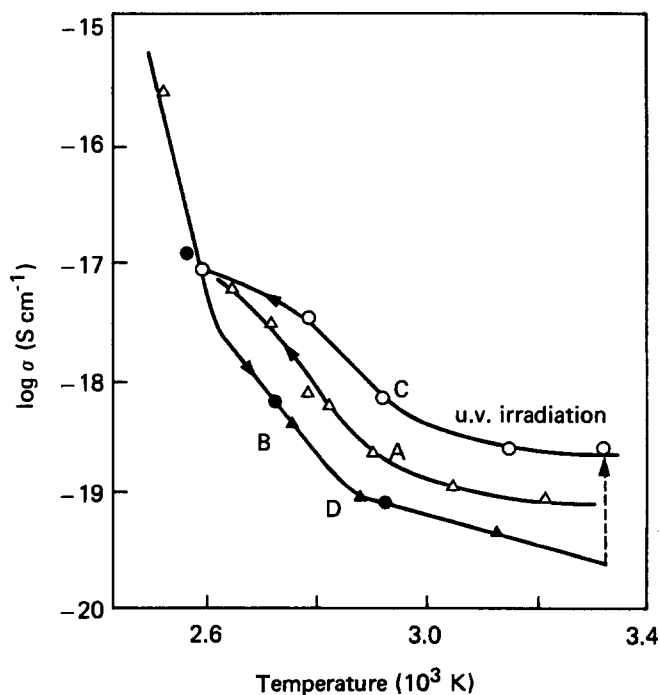

Figure 3 Effect of u.v. irradiation on the temperature dependence of conductivity in the PEN film

Table 1 Dark conduction in PEN film

Temperature range	Activation energy (eV)	Main conduction process
below T_b	0.25	electronic
T_b-T_g	0.80	ionic
above T_g	3.7	ionic

electronic conduction. *Figure 4* shows the temperature dependence of photocurrents in the samples with various degrees of crystallinity obtained by the annealing of the amorphous PEN films at various temperatures. We will discuss the data here from two points of view: the activation energy and the magnitude of the photocurrent.

The variation of both the activation energy of photocurrent and the degree of crystallinity with annealing in PEN films are shown in *Figure 5*. The degree of crystallinity gently increased with increase in annealing temperature up to 420 K, and then showed a drastic increase at around 420 K. However, the activation energy decreased with increase in annealing temperature, giving a strong correlation with the variation of crystallinity. Magnitudes of photocurrent are determined by both photo-generation and carrier transport. The photo-carrier generation, however, can be assumed to include no thermal activation process, whereas the carrier transport in polymers has been known to exhibit activation processes. Therefore, the observed decrease in the activation energy of the photocurrent should be reduced to the reduced activation energy for the carrier transport. In other words, the increase in crystallinity can contribute to the enhancement of carrier mobility via the reduction of the activation energy of transport.

The magnitude of the photocurrent increased with increase in annealing temperature up to 413 K. However, in the sample annealed at 435 K, the photocurrent decreased to half that for the sample annealed at 413 K (*Figure 4*). The activation energy, however, continued to decrease with annealing, even at around the annealing temperature which brought about the decrease in the magnitude of the photocurrent. This suggests that the decrease in photocurrent in the PEN, with high crystallinity, is caused by the suppression of the efficiency of photo-carrier generation, which is related to the crystalline phase of PEN. One possible explanation may be the formation of a large number of excimer sites, which serve as traps for the photo-generated excitons.

Figure 6 shows the fluorescence emission spectra of PEN film excited at 330 nm. The emission peak at 435 nm has been reported to be the fluorescence from the excimer
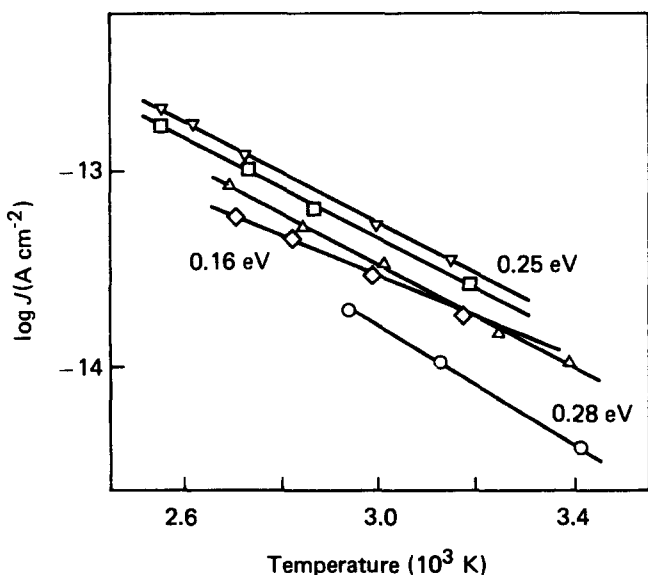

Figure 5 Degree of crystallinity and activation energy of photocurrent plotted against annealing temperature
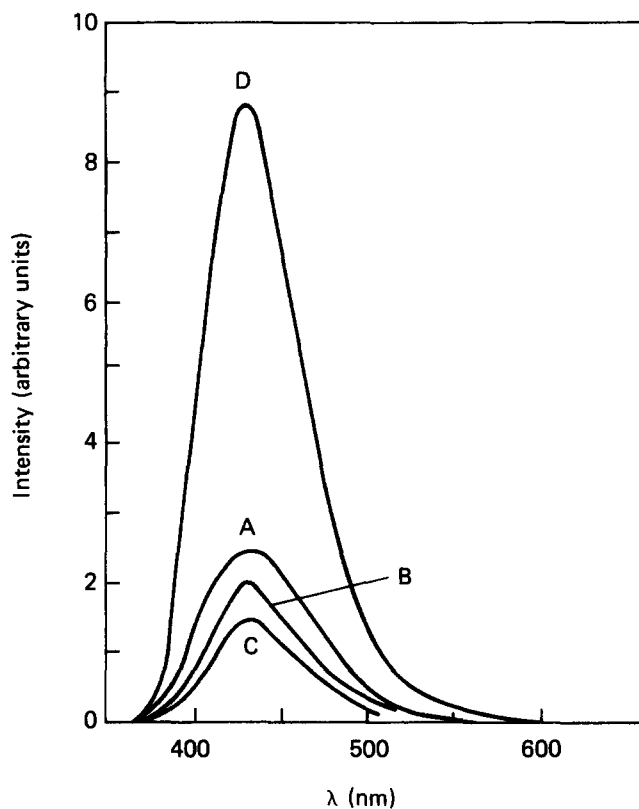
Figure 6 Fluorescence emission spectra of the PEN film with varying crystallinity: annealing temperatures (A) amorphous, (B) 398 K, (C) 417 K, (D) 456 K

states[5,6]. The decrease in fluorescence intensity with annealing up to 417 K could be ascribed to photo-degradation of the PEN[11], since the measurement was carried out successively on the same sample, with intermittent annealing. The fluorescence intensity of the sample annealed at 456 K was, in comparison, about 4 times that of the amorphous samples. This indicates that the large number of excimer sites, which are based on the stacking of naphthalene rings, are formed with the large increase in crystallinity around 435 K. The excimer sites may act as traps for the excitons and reduce the efficiency of photo-carrier generation. The observed photocurrent then turns out to be rather small, even though the activation energy of carrier transport is lowered. Naturally, further studies are required to prove the interrelation between the excimer sites and the carrier generation process in PEN. However, we should point out

Figure 4 Effects of annealing on photocurrent in the PEN film: annealing temperatures (O) amorphous, (△) 386 K, (□) 400 K, (▽) 413 K, (◇) 435 K

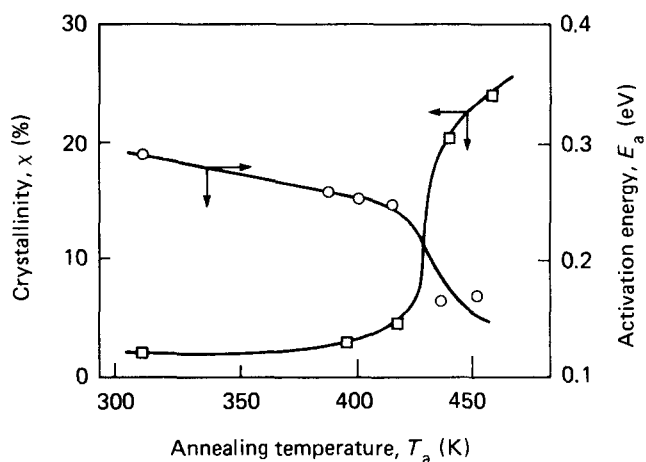here that higher-order structures seem to largely influence the photo-carrier generation process as well as the carrier transport process.

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