Thermally stimulated currents in undoped poly(*p*-phenylene vinylene) and the effect of stretching

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Abstract. Thermally stimulated current (TSC) measurements have been performed on undoped stretched poly(*p*-phenylene vinylene) (PPV). Two TSC peaks P_1 and P_2 are observed and become smaller as the stretching ratio was gradually increased. The trap depths are evaluated from the initial increasing part of each separated peak by the thermal cleaning method to be about 0.36 eV and 0.55 eV for peaks P_1 and P_2, respectively, regardless of the stretching ratio. However, the second peak P_2 is markedly suppressed on stretching. Peak P_1 is interpreted as originating from electron traps formed by impurities such as a bromine (Br_2) or sulphur trioxide (SO_3) which were not eliminated by heat treatment. In contrast, peak P_2 was confirmed to be based on defects already existing in the amorphous parts of PPV since the crystallinity in PPV increases and the spin density evaluated by integration of the electron spin resonance spectra in stretched PPV decreases on increasing the stretching ratio.

1. Introduction

Recently, a conducting polymer with a molecular structure of a highly extended conjugated π-electron system has attracted much attention for both fundamental and practical reasons because in this polymer an insulator–metal transition was induced on doping of acceptors or donors.

Until now, polyacetylene $(CH)_x$ has been one of the most extensively studied conducting polymers, since it was synthesised at an early stage in the development of conducting polymers and its has the most simple molecular structure. The properties of $(CH)_x$ are explained by the introduction of soliton and charged soliton models (Su *et al* 1979).

In contrast, polarons and bi-polarons have been considered to play important roles in several conducting polymers with non-degenerate molecular structures such as polypyrrole (Scott *et al* 1983, Brédas *et al* 1984), polythiophene (Kaneto *et al* 1984, Tourillon *et al* 1984, Kobayashi *et al* 1984), poly(*p*-phenylene) (Chance *et al* 1984, Kispert *et al* 1984) and poly(*p*-phenylene vinylene) (PPV) (Yoshino *et al* 1986, Bradley 1987).

Thus the properties of conducting polymers vary widely with a small difference in their molecular structures. The electrical, optical and magnetic properties of conducting polymers are also strongly affected by various types of defect. Solitons, charged solitons, polarons, bi-polarons, etc, are also regarded as types of defect in the conjugated double

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bond. The measurement of thermally stimulated currents (TSCs) is one of the most effective methods for investigating defects in polymers.

The elongation of polymer films also has a remarkable influence on the property of the conducting polymer. In our previous paper, observations of TSC signals in $(CH)_x$ and polychlorophenylacetylene were described (Yoshino *et al* 1981, Onoda *et al* 1986). However, the origin of the TSC peaks has not been clarified in detail. The effects of molecular structure and elongation on trap states of TSCs have not been clarified also until now.

Recently, a method for preparation of high-quality conducting PPV films via pyrolysis of a water-soluble precursor polymer of a sulphonium salt has been developed by Murase *et al* (1984). The electrical conductivity, electron spin resonance (ESR) spectra, optical absorption spectra of PPV and their dependences on doping have been studied in detail and these properties are interpreted in terms of polaron or bi-polaron models (Yoshino *et al* 1986).

In contrast, PPV can also be highly stretched, resulting in anisotropic electrical and optical properties (Takiguchi *et al* 1987). This type of PPV has also attracted much attention as a precursor for the preparation of highly conductive graphite film (Ueno and Yoshino 1986). In a recent paper, we reported on the TSCs in unstretched PPV and its doping effects (Onoda *et al* 1988a, b). However, the TSC properties in stretched PPV have not been clarified. From the viewpoint as described above, it is very interesting to investigate the TSC properties of stretched PPV films.

In this paper, we report TSC measurements in undoped PPV films as a function of stretching ratio.

2. Sample and experimental details

PPV films were prepared by the method of Murase *et al* (1984), i.e. a polyelectrolyte was derived by adding an ion-exchanging resin (Amberlite) to *p*-xylene(diethylsulphonium bromide) dissolved in distilled water. A precursor film was prepared by casting from the aqueous solution of the polyelectrolyte; then the film was subjected to a heat treatment at 200 °C for 1 h under an Ar atmosphere. By this procedure, an unstretched PPV film was obtained.

Stretching of the films was carried out as follows. The precursor film of the poly-electrolyte of sulphonium salt was stretched to an arbitrary length under an Ar atmosphere at 100 °C, and then it was heat treated at 200 °C for 1 h under an Ar atmosphere. The stretching ratio l/l_0 is the ratio of drawn length l to undrawn length l_0.

Figure 1 shows a schematic diagram of the synthesis of PPV.

The ESR measurements were performed with a Bruker ESP 300 spectrometer in the X band at room temperature. 1,1-diphenyl-2-picryl-hydrazyl (DPPH) was used to estimate the unpaired spin density. All ESR spectra were measured at low microwave power (20 μW) and integrated twice using a digitiser connected to a microcomputer.

Films about 10 μm in thickness with an Au-evaporated electrode 0.6 cm in diameter with a guard ring on both surfaces were used as samples.

The TSCs were measured by the conventional technique used for insulating polymers as follows (Turnhout 1975). First, a DC voltage was applied to the undoped stretched PPV film at 30 °C for 1 h and the charging current was measured with a multi-channel electrometer (Keithley 610C). Then the sample was cooled to about −70 °C while maintaining the bias voltage. After short-circuiting the sample until the discharging
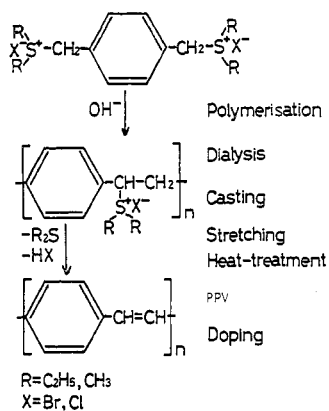
Figure 1. Schematic diagram of the synthesis of PPV: $R \equiv C_2H_5$, CH_3; $X \equiv Br$, Cl.

current became negligible, the sample was heated at a constant rate β of $2\,^{\circ}C\,min^{-1}$ in order to measure the TSC through a short circuit with a multi-channel electrometer. These experiments were carried out under a vacuum of about 10^{-5} Torr.
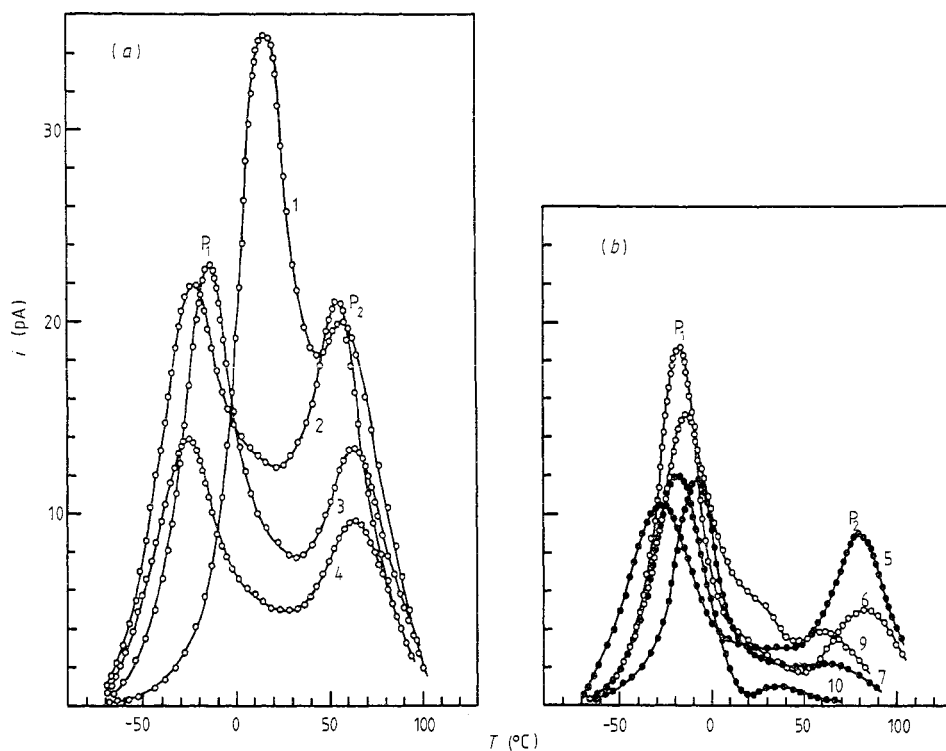

Figure 2. TSC(i) spectra for various stretching ratios l/l_0 (given on curves) of PPV polarised at $100\,kV\,cm^{-1}$ and $30\,^{\circ}C$: (a) relatively small ratio; (b) large stretching ratio.

3. Results and discussion

Figure 2 shows the TSC spectra for various stretching ratios l/l_0 of PPV polarised at 100 kV cm^{-1}. A sample heated once to about 100 °C and cooled without a bias voltage did not produce such a current during a second heating cycle. This clearly indicates that the observed current is the usual TSC. As is obvious from figure 2, two TSC peaks P_1 and P_2 were observed at around 20 and 50 °C in unstretched PPV and at around -20 and 50 °C in stretched PPV. These peaks gradually became smaller as the stretching ratio was increased. In particular, peak P_2 became extremely small. These peaks were separated using the thermal cleaning method as follows. When the temperature exceeded the first peak (P_1), the sample was rapidly cooled to about -70 °C. During the second heating cycle, no detrapping current from the trap corresponding to peak P_1 appeared. Then we could observe the TSC peak originating only from the second peak (P_2).
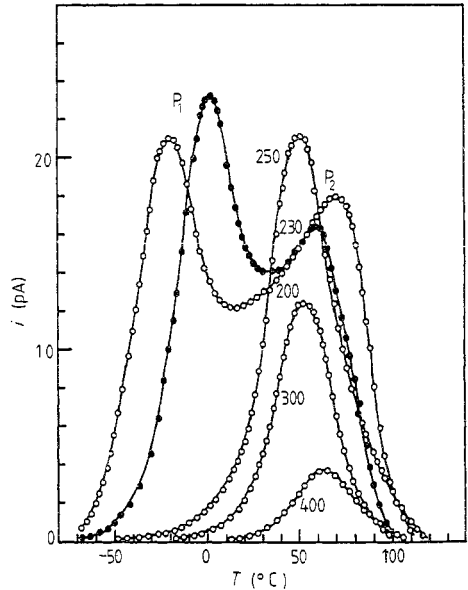
The trap depths were evaluated from the Arrhenius plot of $\log i$ against $1/T$ of the initial increasing part of each separated peak to be about 0.36 eV and 0.55 eV for peaks P_1 and P_2, respectively, regardless of the stretching ratio.

We cannot definitely determine the origin of traps from the results in this experiment. To clarify the localised centre responsible for peak P_1, we carried out the following experiments.

Figure 3 shows the TSC spectra for various heat treatment times t_{HT} at 200 °C on the unstretched PPV film polarised at 100 kV cm^{-1}. For a short t_{HT}, the two TSC peaks P_1 and
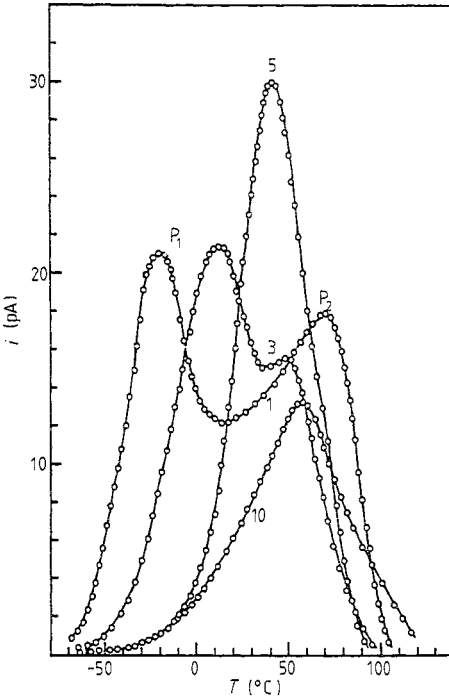

Figure 3. TSC(i) spectra for various heat treatment times t_{HT} (given on curves in h) at 200 °C for unstretched PPV film polarised at 100 kV cm^{-1} and 30 °C.

Figure 4. TSC(i) spectra for the PPV sample heat treated for 1 h at various temperatures T_{HT} (given on curves in °C).

P_2 are observed. Peak P_1 moves to higher temperatures as t_{HT} was increased. However, peak P_2 does not move significantly. The trap depths were evaluated from the initial increasing part of each separated peak by the thermal cleaning method to be 0.34 eV and 0.56 eV for peaks P_1 and P_2, respectively. However, as t_{HT} was increased further, only a single peak was observed and this peak was also suppressed on increasing t_{HT} even more. The trap depth of this remaining peak was evaluated to be about 0.36 eV. Accordingly, we can conclude that the single TSC peak remaining in the sample for a long t_{HT} (at 200 °C) corresponds to peak P_1 previously recorded.

Figure 4 shows the TSC spectra in the sample heat treated for 1 h at various temperatures T_{HT}. When T_{HT} was low, the two TSC peaks P_1 and P_2 were observed. Peak P_1 moves to higher temperatures as T_{HT} was increased. However, peak P_2 does not move noticeably. The trap depths were evaluated from the initial increasing part of each peak separated by the thermal cleaning method to be about 0.34 eV and 0.55 eV for peaks P_1 and P_2 respectively. However, as T_{HT} was increased further, a single peak was observed. Although these peaks for samples with $T_{HT} > 250$ °C appear in a similar temperature range, the activation energy of the initial increasing part differed markedly, as is evident in figure 5. For $T_{HT} = 250$ °C, since the trap depth was evaluated to be about 0.35 eV,
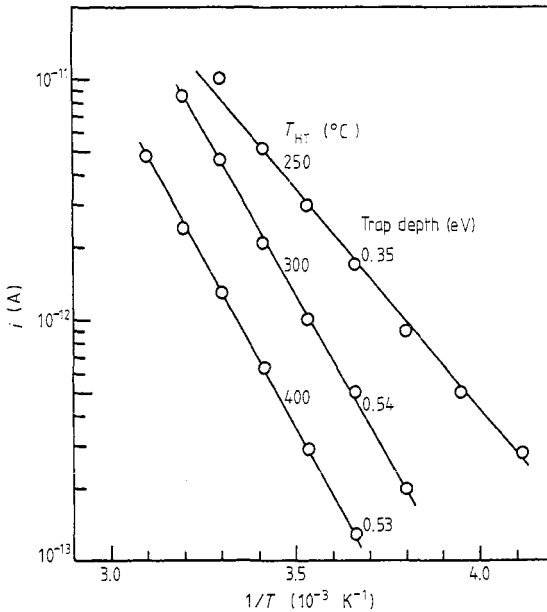
Figure 5. Arrhenius plots of the initial increasing part of the TSC spectra in a PPV sample heat treated above 250 °C.

the TSC peak which can be interpreted to have originated from peak P_1 appears. In contrast, for T_{HT}-values of 300 and 400 °C, the trap depth was evaluated to be about 0.54 eV, suggesting that the TSC peak corresponds to peak P_2. Thus, when T_{HT} becomes high enough, peak P_1 disappears and peak P_2 remains, and its energy decreases on increasing the temperature further.

Figure 6 shows the TSC spectra in unstretched PPV films 5 and 20 μm thick. In this case, PPV films were heat treated at 200 °C for 22 h. For PPV films 20 μm thick, peak P_1 was observed at around 20 °C and a shoulder in peak P_2 was observed at around 50 °C. However, for PPV films 5 μm thick, only peak P_2 was observed at around 50 °C and the TSC peak originating from peak P_1 did not appear, which suggests that the traps corresponding to peak P_1 can be easily removed in the thin sample.
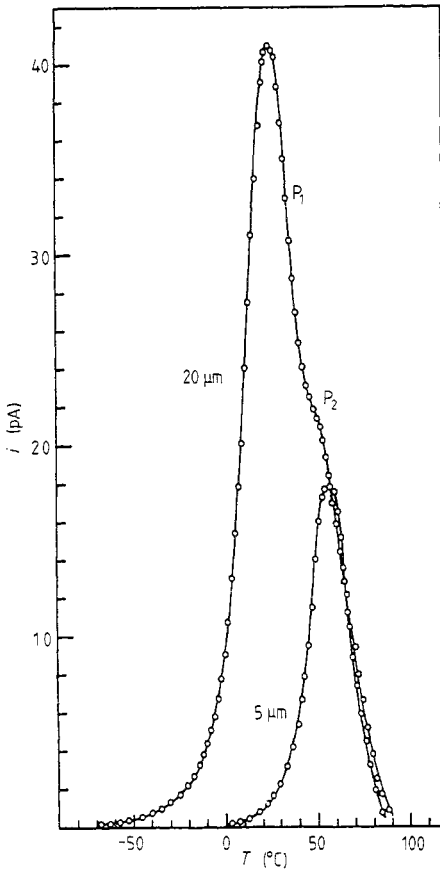
Figure 6. TSC(i) spectra in unstretched PPV films 5 and 20 μm thick. In this case, PPV films were heat treated at 200 °C for 22 h.

As discussed above, the effects of the temperature and time of the heat treatment on TSCs are very complicated. To interpret this complicated behaviour, a study on the influence of dopants on TSCs in PPV was carried out.

In our previous paper, we reported the TSC spectra in iodine (I_2)-doped unstretched PPV heat treated at 300 °C for 1 h (Onoda *et al* 1988a, b). Figures 7(a) and 7(b) show the TSC spectra of I_2-doped PPV films for a relatively short doping time and for a long doping time, respectively. As is evident from figure 7(a), the TSC peak of undoped PPV was observed at around 60 °C. The trap depth was evaluated as about 0.5 eV, which corresponds to peak P_2. This peak became larger as the doping time was increased and
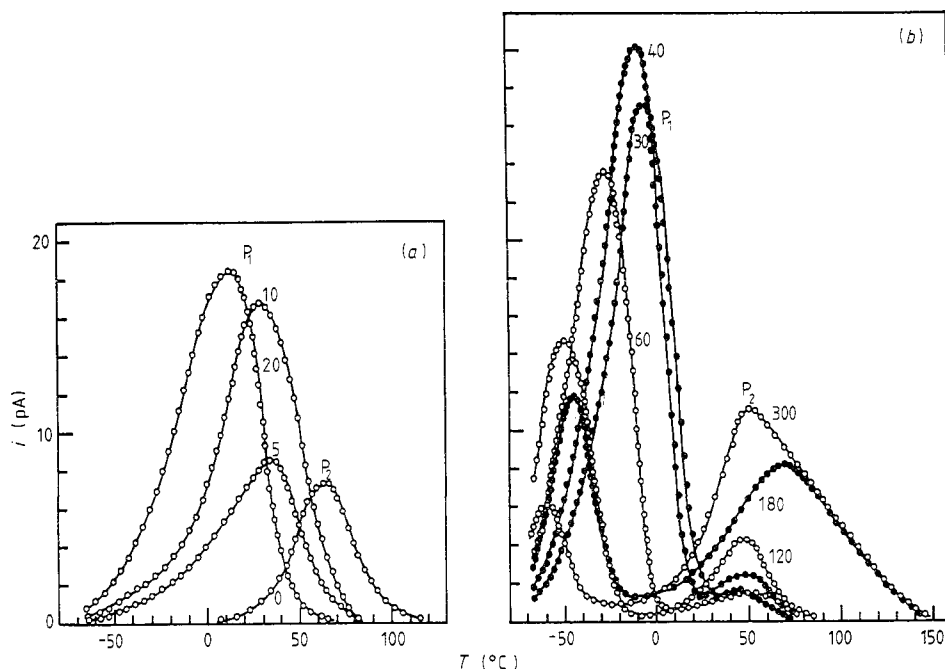
Figure 7. TSC(i) spectra of PPV doped with I_2 for various doping times t_d (given on curves in min) polarised at 100 kV cm^{-1} and 30 °C: (a) relatively short doping time; (b) long doping time.

gradually shifted to the low temperatures apparently on increasing the I_2 concentration. However, it should be mentioned that the trap depth of the slightly doped sample evaluated by determining the initial increasing part of the peak is much less than that of the undoped sample. The peak in the doped sample seems to correspond to peak P_1 in figure 2. For a much longer doping time, the two TSC peaks P_1 and P_2 were observed, as shown in figure 7(b). Peak P_1 shifts to the low temperatures on increasing the I_2 concentration. Peak P_2 at around 50 °C became larger on increasing the I_2 concentration and was observed at nearly the same temperature as the peak in the undoped PPV. It is assumed that peak P_1 originates from electron traps formed by the effect of doped I_2 molecules. Moreover, it is considered that the localised centre related to the peak in undoped PPV and to peak P_2 in I_2-doped PPV exits in undoped as-grown PPV originally. Thus, it is clear that the intensity and the temperature of peak P_1 in I_2-doped PPV drastically changed owing to the amount of dopant. Although the detailed mechanism and origin of the formation of shallow traps corresponding to peak P_1 are not clear at this stage, we can at least conclude that P_1 is closely related to the dopant.

From the above experimental results, it is clear that peak P_1 observed in figures 3, 4 and 6 shows the same behaviour as peak P_1 of I_2-doped PPV in figure 7. From the method of synthesis used to prepare PPV, it is considered that impurities which were not eliminated by heat treatment play a role in the formation of the localised centre responsible for peak P_1, and a dopant such as bromine (Br_2) or sulphur trioxide (SO_3) which can be formed during the heat treatment of precursor polymer films may have predoped the films accidentally. Accordingly the localised centre causing peak P_1 obtained in figure 2 may be interpreted as due to impurities (Br_2, SO_3, etc).

Figure 8 shows the relation between the stretching ratios and the integrated net TSC charge of peak P_2 separated by applying the thermal cleaning method. This net TSC charge of peak P_2 strongly decreased on increasing the stretching ratio and, in the PPV film stretched tenfold ($l/l_0 = 10$), it was reduced by about an order of magnitude in comparison with the unstretched PPV ($l/l_0 = 1$).
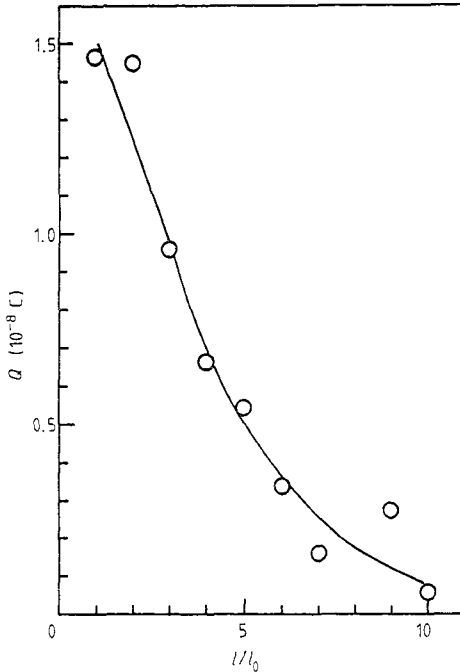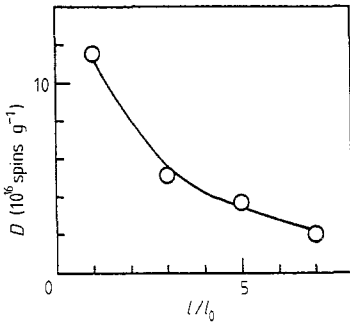

Figure 8. Relation between the stretching ratios (l/l_0) and the integrated net TSC charge (Q) of peak P_2 for PPV separated by applying the thermal cleaning method.
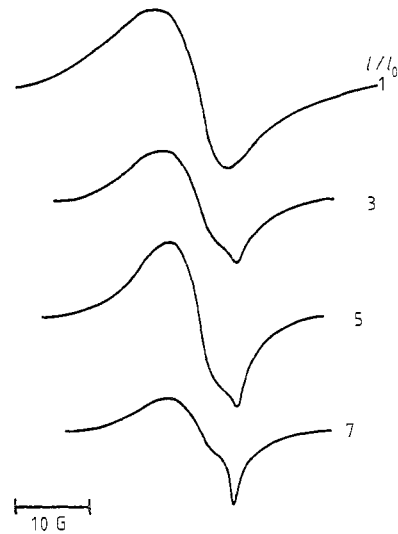
Figure 9. ESR spectra of the samples with various stretching ratios at room temperature.

The ESR spectra of the samples with various stretching ratios at room temperature are shown in figure 9, where the dimensions of the horizontal axis are equal for all spectra. The spectrum of unstretched PPV is nearly symmetric with a linewidth of about 8 G and considered to be derived from neutral defects (Onoda *et al* 1988a, b). As the stretching ratio increases, the signal intensity gradually decreases and it should be noted that a new sharp component appeared and increased at higher stretching ratios. Details of the ESR spectra are not clear at this stage. However, this new sharp component is considered to be closely related to the mobile carrier. The crystallinity in PPV has been confirmed to increase with increasing stretching ratio (Murase *et al* 1984, Bradley 1987). Therefore, this result could be due to the fast carrier migration in the increasingly crystalline regions of the stretched PPV.

Figure 10 shows the relation between the spin density evaluated from integration of the ESR spectra in figure 8 and the stretching ratio. As is evident from this figure, the spin density gradually decreases on increasing stretching ratio, and the spin density of PPV

Figure 10. Relation between the spin density (D) evaluated by integration of the ESR spectra in figure 8 and the stretching ratio (l/l_0) for PPV.

stretched sevenfold ($l/l_0 = 7$) becomes smaller by about an order of magnitude than that of unstretched PPV ($l/l_0 = 1$).

The decrease in the spin density by the stretching indicates a decrease in the defects initially present in PPV.

In our previous paper, we speculated that the localised centre of peak P_2 for unstretched PPV is a defect originally existing in PPV (Onoda *et al* 1988a, b). Moreover, it has already been reported that the crystallisation of PPV also increases with increasing T_{HT} (Murase *et al* 1984, Bradley 1987), resulting in the transformation of the amorphous part of the PPV to a crystalline state. As shown in figures 2 and 4, peak P_2 decreased on increasing the stretching ratio and also T_{HT}. Accordingly, it could be that the amorphous parts of the PPV acts as localised centres. That is, the localised centre of peak P_2 is due to existing defects in the amorphous parts of PPV.

The formation of highly graphitised film from stretched PPV but carbonised film from unstretched PPV (Ueno and Yoshino 1986) may be related to the decreased amorphous region and the lower density of defects in the stretched PPV film, as observed in our experiments.

4. Summary

TSC measurements have been carried out on undoped stretched PPV films. The results of this study can be summarised as follows.

Two TSC peaks P_1 and P_2 were observed at around 20 and 50 °C for unstretched PPV and at around -20 and 50 °C for stretched PPV. These peaks became smaller as the stretching ratio was gradually increased. In particular, peak P_2 became negligibly small at high stretching ratios. The trap depths were evaluated from Arrhenius plots of log i against $1/T$ of the initial increasing part of each separated peak to be about 0.36 eV and 0.55 eV for peaks P_1 and P_2, respectively, regardless of the stretching ratio l/l_0. The spin density evaluated from integration of the ESR spectra gradually decreases with increasing stretching ratio. The decrease in the spin density due to stretching indicates a decrease in the defects in PPV. It is considered that peak P_1 originates from electron traps formed by the effect of impurities such as Br_2 or SO_3 which are formed during the heat treatment of the precursor polymer films. Moreover, the localised centre corresponding to peak P_2 in figure 2 is interpreted as due to the existing defects in the amorphous parts of PPV originally, which can be suppressed by stretching or high-temperature treatment.

Acknowledgments

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