Switching in Poly-*N*-vinylcarbazole Thin Films Effect of Molecular Weight and Impurities

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ABSTRACT: In order to elucidate the trapping sites which serve an important role in the switching of poly-*N*-vinylcarbazole (PVCz), the effects of the molecular weight and the method of polymerization on the threshold voltage of switching was studied. The trap density was also determined from the threshold voltage. Polymerization was initiated by α,α′-azobisisobutyronitrile (AIBN) or γ-ray irradiation. The trap density was larger for lower molecular weight PVCz than for higher molecular weight materials. PVCz prepared by AIBN initiator had a trap density larger than that made by γ-ray initiation when both polymers had the same molecular weight. Doping of iodine onto PVCz increased the trap density; however, doping of tetramethyl-*p*-phenylenediamine or 1,5-diaminonaphthalene had no such effect. Heat treatment of PVCz seemed to have some effect on the switching characteristics.
    KEY WORDS   Poly-*N*-vinylcarbazole / Switching / Trap Density /

A sudden change from a high to a low resistance state when a voltage is applied has been observed in many inorganic materials such as chalcogenide glasses and oxides. This phenomenon is called switching. In recent years, switching in thin organic polymer films has also been reported by several authors.[1-7] Switching in these reports is classified into two categories on the basis of the mechanisms involved. The first group is caused by Joule heating through a filamental path; in the second group, an electronic mechanism predominates.

In our previous paper,[5] switching in thin poly-*N*-vinylcarbazole films was interpreted in terms of the simplified trap-filled limited conduction. In the present study, the effect of molecular weight and the type of initiation of polymerization on switching characteristics was investigated so as to provide evidence for our previous interpretation in which traps played an important role in switching. The effect of doping of several electron donors was also studied.

EXPERIMENTAL

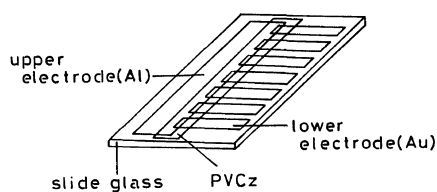Four different poly-*N*-vinylcarbazole (PVCz) materials were prepared under different conditions and are listed in Table I. Radiation-induced polymerization was carried out with ^{60}Co at the Japan Atomic Energy Research Institute in Tokai. The catalytic polymerization was initiated by azobisisobutyronitrile (AIBN) in a benzen solution. All PVCz materials were purified twice by precipitation from a benzene solution using methanol as the precipitant. Molecular weight was determined from viscosity.

A gold electrode deposited on a glass plate by vacuum evaporation was dipped into a benzene solution of PVCz and dried slowly. The upper electrode, aluminum, was then deposited in vacuum on the PVCz film. The sandwich type cell thus prepared is shown in Figure 1. The film thickness was determined by the measurement of the capacitance. The circuit for the switching measurement was the same as that reported in the previous paper.[5]

In the present study, thermally stimulated current (TSC) was recorded for PVCz which had been converted to the on-state by an applied voltage higher than the threshold voltage V_{th}. The temperature of the sample in the on-state was raised from room temperature to 140°C at a constant rate using a thermal program controller (Shinku Riko HPC
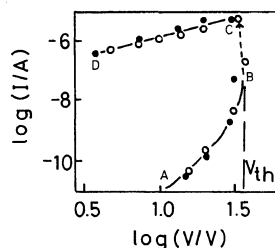
Table I. Conditions of polymerization

No.	Initiation	Conditions	Molecular weight
1	γ-Rays	$6.6 \times 10^4 \, \text{R} \, \text{h}^{-1}$, 30°C, 240 h	6.0×10^4
2	γ-Rays	$6.6 \times 10^4 \, \text{R} \, \text{h}^{-1}$, 60°C, 16 h	5.3×10^5
3	AIBN	(Catalyst 0.006 mol + monomer 1.5 mol)/1 benzene, 70°C, 3 h	2.0×10^5
4	Commercial	Tokyo Kasei Kogyo	1.6×10^6

Figure 2. Switching characteristics of PVCz. V_{th}, threshold voltage. AB, off-state; CD, on-state. ○ and ● are the results obtained from different cells on the same glass substrate.

Figure 1. Sandwich type cell.
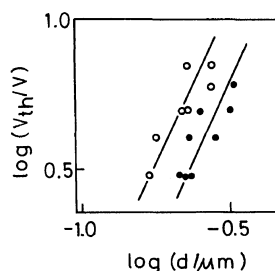
Figure 3. Logarithmic plot of threshold voltage (V_{th}) against film thickness (d). ○, molecular weight 6.0×10^4; ●, 5.3×10^5; both PVCz materials were polymerized with γ-rays.

5000). The current due to the released charges was recorded on a multi-pen recorder through a picoammeter. The temperature was also recorded simultaneously on the same recorder. TSC was also measured for the PVCz into which carriers had been injected by UV illumination with a mercury lamp.

RESULTS AND DISCUSSION

Typical switching characteristics are given in Figure 2. In the low voltage range, the current was extremely small (off-state). When the voltage was high, the current obeyed the square law until reaching the threshold voltage where the current commenced to rise steeply and the sample converted to the on-state (low resistance state). The on-state was relatively stable, lasting more than a day at room temperature. However, the sample easily resumed to the off-state when heated or exposed to light. This switch-on and turn-off could be repeated without any damage to the sample which was checked with a scanning electron microscope following the switching. This differs considerably from other reports in which dots or breaks caused by Joule heating along the filamentary conductive paths were observed. In these reports, the formation of filaments of carbonized polymers caused a low resistance state (on-state). The on-state could be erased by applying a

pulsed current through the sample. In the present study, the high resistance (1M—10MΩ) connected in series with the sample limited the current so that no breakdown occurred when a large amount of current was applied. The injection of carriers was maintained to a certain extent, causing most of the traps to become filled.

Patora et al.[8] first related the V–I characteristics of PVCz to the results of TSC measurement. The energy trap level densities estimated by the two different methods were in fairly good agreement with each other. Kryszewski[9] reported that in the dark, high molecular weight PVCz exhibits a higher conductivity than lower molecular weight material, suggesting that the chain ends are trapping sites.

As described in the previous paper,[5] in the switching of PVCz films, transition to the on-state from the off-state may be caused by the formation of a trapfilled state if it is assumed that in the off-state, the current obeys the SCLC conduction mechanism. Assuming the uniform energy distribution of shallow traps, the voltage at which the traps are filled is

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expressed as $V_{TFL} = ed^2 N_t/2\varepsilon$,[10] where e is the electronic charge, d, the film thickness, N_t, the trap density and ε, the dielectric constant. If V_{TFL} corresponds to the threshold voltage V_{th}, the observed V_{th} must be proportional to the square of the film thickness. Figure 3 indicates that the logarithmic plot of V_{th} against d has a slope of 2. In addition, Figure 3 shows that the V_{th} depends on the molecular weight of the PVCz. The higher molecular weight PVCz has a lower threshold voltage than the lower molcular weight PVCz. This suggests that the chain ends of the PVCz act as shallow traps, so that N_t is related to the number of chain ends as Kryszewski suggested.[9]

Traps can be formed not only physically but chemically as well. Iodine was chosen as a chemical impurity and may form a trap in PVCz. Three mole percent of I_2 were added to the PVCz solution before deposition of the PVCz onto the slide glass. The PVCz doped with I_2 was used as a switching sample. The N_t value for the doped PVCz calculated from the observed V_{th} using equation $V_{th} = ed^2 N_t/2\varepsilon$ is twice as large as that of undoped PVCz. The dark conductivity increased by a factor of two in I_2 doped PVCz. Hermann and Rembaum[11] observed the sign discrepancy of the carrier in the PVCz–I_2 complex in the study of its Hall and Seebeck effects. It seems that in the case of PVCz–I_2 complex, the negative carrier should not be neglected in some circumstances. However, further work must be done to understand the role of I_2 in PVCz. On the other hand, two electron donating dopants, *i.e.,* tetramethyl-*p*-phenylenediamine (TMPD) and 1,5-diaminonaphthalene (DAN), have no effect on the switching characteristics. According to Okamoto *et al.,*[12] TMPD and DAN form deep traps in PVCz, decreasing the hole current significantly in photoconduction. In the present study, the dark conductivity decreased when 6 mol% of TMPD or DAN was doped in PVCz. However, no appreciable effect of the doping of these materials on the value of V_{th} was observed. Another possible chemical trap in the polymer is a fragment of catalyst bonded at the polymer chain end. As shown in Table II, two different PVCz materials from different origins were compared, *i.e.,* one prepared by γ-ray-induced polymerization and the other by catalytic polymerization. The trap density for the catalytically polymerized PVCz is larger than that for PVCz made by γ-ray irradiation, though the former PVCz has

Table II. Trap density

No.	Molecular weight	Trap density cm^{-3}	
		from V_{th}	from TSC
1	6.0×10^4 (γ-rays)	9.9×10^{16}	7.7×10^{17}
2	5.3×10^5 (γ-rays)	5.7×10^{16}	7.0×10^{16}
3	2.0×10^6 (AIBN)	2.6×10^{17}	2.6×10^{19}

a higher molecular weight than the latter. It is concluded that the fragment from azobisisobutyronitrile at the end of the polymer chain acts as a shallow trap.

In order to compare the trap density for the PVCz materials from different origins, a TSC measurement was carried out. The carrier was injected into the PVCz film by exposing the electrode to light from a high pressure mercury lamp for 20 minutes with an applied field 6×10^5 V cm^{-1} at 120°C, followed by cooling to room temperature. The current due to the released charge was then recorded when the temperature was raised at a constant rate with an applied field of 2×10^4 V cm^{-1}. The results of TSC measurement also indicate that the high molecular weight PVCz has a lower trap density than the low molecular weight materials, and that the catalyst fragment seems to form an effective trapping site as shown in Table II. The values of trap density obtained by the two different methods do not coincide with each other. This may be due to the different conditions under which the carrier injection was carried out at the electrode (dark or UV illuminated) and/or the difference in applied voltages when the carriers were trapped. Kryszewski[9] reported that the pre-illuminated PVCz shows higher conductivity than the non-illuminated one due to the partial filling of traps by light. In the present study, the photoinjection prior to TSC measurements must result in filling more traps than injection in the dark in switching measurements. In addition, the threshold voltage in switching is much higher than the voltage applied for the photoinjection in the TSC measurements.

After the sample had been converted to the on-state, the temperature was raised at a constant rate until no current flowed due to the released charge. The heat-treated sample was found to be in the off-state. The switching and the TSC measurements
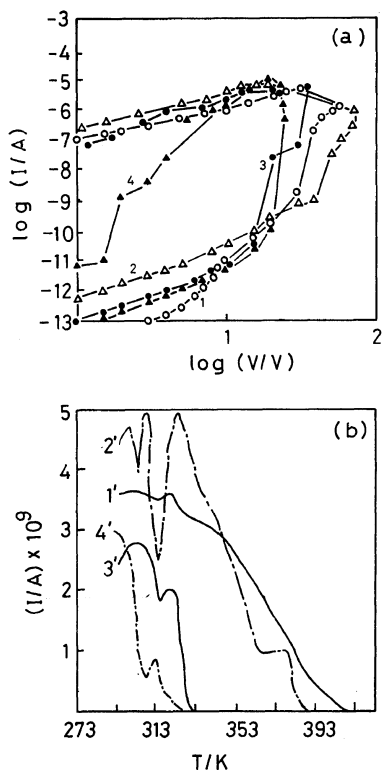
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Figure 4. Repeated switching and TSC measurements. The numbers (1, 2, 3, 4 and 1′, 2′, 3′, 4′) in the figures indicate the run order. (a) Switching: ○, first run; △, after TSC 1′; ●, after TSC 2′; ▲, after TSC 3′. (b) TSC.

were repeated four times. The results are shown in Figure 4. Figure 4(a) shows the switching patterns and Figure 4(b), the TSC curves. Curve 1′ in Figure 4(b) was obtained with the sample in the on-state of curve 1 in Figure 4(a). After the first run of the TSC measurement (curve 1′), switching curve 2 was obtained, followed by the second run of TSC measurements (curve 2′) and so on. The TSC curves in Figure 4(b) suggest that the amount of released charge decreased as the switching on and heating were repeated. Eventually memorization of the on-state became difficult and the switching pattern changed to that of threshold switching. This phenomenon is attributed to the increase in crystallinity as a result of repeated heat treatment during TSC measurements. It was reported by Okamoto et al.[13] that the photocurrent increases with an increase in crystallinity. Okumura and Griffith[14] also reported that the hole mobility increased on heat treatment

of PVCz. In the present investigation, it seems that the possibility of detrapping holes in the on-state increases with an increase in crystallinity, because the heat-treated PVCz provides poor memory characteristics and has a small amount of trapped charges as shown in Figure 4.

CONCLUSIONS

Typical memory switching was observed in PVCz films. The current-voltage characteristics of PVCz film can be explained by the SCLC mechanism. The threshold voltage V_{th} of switching seems to correspond to the trap-filled voltage V_{TFL}, going on the assumption that there is a single distribution in the energy of shallow traps.

Chemical impurities such as tetramethyl-p-phenylenediamine and 1,5-diaminonaphthalene do not affect the switching characteristics, although they are capable of forming deep traps in PVCz. On the other hand, the chain ends of PVCz, particularly the fragments of the initiator, act as a trap to control the threshold voltage V_{th}.

The crystallinity affects the duration of the memory state. Amorphous PVCz is mor favorable for memory switching than crystallized PVCz.

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