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Switching in polystyrene and polymethyl methacrylate thin films: effect of preparation conditions of the polymers

Y. SAKAI, Y. SADAOKA, G. OKADA
Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790, Japan

Switching without any break in the electrodes was observed in polystyrene and polymethyl methacrylate films by controlling the current using a high resistance connected in series with the sample. The effect of the method of polymerization on the switching characteristics were studies for both polymers. Polymers were prepared by γ-ray irradiation or by catalytic or noncatalytic thermal polymerization. The switching characteristics gave poor reproducibility for the catalytically polymerized polystyrene, but no difference was observed for the three types of polymethyl methacrylate from different origins. In the case of polystyrene, the lower the molecule weight, the higher was the threshold voltage. With polymethyl methacrylate such a dependence was not observed. In both polymers the on-state is relatively stable. When the samples in the on-state were heated above 100° C, they were converted to the off-state. No dots or breaks on the sample were detected by scanning electron microscopy (SEM) after switching has occurred.

1. Introduction

In recent years switching in organic polymer films has been reported by several authors [1–7]. In polystryene films memory switching accompanied by damage of the film and the electrodes has been observed [1–4]. This switching may be the result of pyrolysis or partial decomposition of the films by Joule heating through the filamental paths. On the other hand, an electronic mechanism without damage to the films was suggested by Sadaoka and Sakai [5] and Henisch and Meyers [6] in polyvinylcarbazole and polymethyl methacrylate films, respectively. In the present work, memory and threshold switching without damage to polymer films were observed in polystyrene (PST) and polymethyl methacrylate (PMMA) films. The thermally stimulated current (TSC) was also measured after they had been converted to the on-state, so as to estimate the amount of the trapped charges in the films.

2. Experimental procedure

Eight PST and five PMMA samples were prepared under different conditions. These are listed in Tables I and II. All the polymers except commercial PST were prepared in our laboratory. The catalytic polymerization was initiated by the use of azobisisobutyronitrile (AIBN) in benzene solution. The radiation-induced polymerization was carried out with ^{60}Co at the Japan Atomic Energy Research Institute at Tokai. All the polymers thus prepared were then purified three times by precipitation from benzene solution using methanol as a precipitant. The molecular weights were calculated from the viscosity.

Polymer film was prepared by deposition from a solution of benzene onto a gold electrode which had previously been prepared by vacuum evaporation onto a glass plate. After the solvent had been slowly evaporated, an aluminium electrode was deposited on top of the film by vacuum evaporation. On each glass plate, thirty cells were pre-

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TABLE I Polystyrene

Number	Initiation	Conditions of polymerization	Molecular weight
1	commercial	Wako Pure Chemical Industries Inc.	2.5×10^5
2	catalytic	1 mol monomer + 0.1 g AIBN in 1 l benzene solution, at 100° C 6 h	2.6×10^4
3	catalytic	5 mol monomer + 0.1 g AIBN in 1 l benzene solution, at 65° C 6 h	2.2×10^5
4	γ-ray induced	intensity 2.4×10^5 R/h 2 h at 60° C	5.5×10^5
5	γ-ray induced	intensity 2.4×10^5 R/h 2 h at 60° C, postpolymerized for 10 days	2.2×10^6
6	noncatalytic	at 97° C; 5 h	5.1×10^5
7	noncatalytic	at 35°C; 16 days	2.7×10^6

TABLE II Polymethyl methacrylate

Number	Initiation	Conditions of polymerization	Molecular weight
1	catalytic	5 mol monomer + 0.1 g AIBN in 1 l benzene solution at 100° C 2 h	6.6×10^5
2	γ-ray induced	intensity 3.5×10^4 R/h 1 h at room temperature	7.1×10^4
3	γ-ray induced	intensity 9.1×10^5 R/h 10 min at room temperature	9.1×10^5
4	noncatalytic	at 150° C 8 h	2.8×10^6
5	noncatalytic	at 60° C 48 h	1.1×10^7

pared. In most cases two plates were prepared for each polymer from a different origin. The sixty cells for each polymer were used for switching measurements. The thickness of the polymer film was determined by the measurement of capacitance.

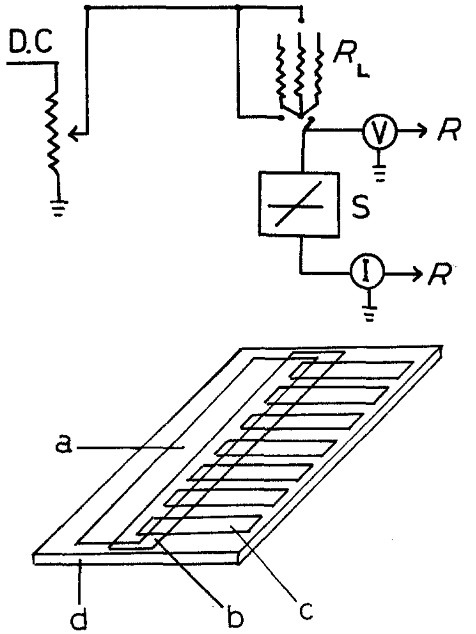

Figure 1 Schematic illustration of the cell and the circuit for switching measurements. a – upper electrode (Al), b – polymer film, c – lower electrode (gold), d – glass substrate, D.C. – d.c. power supply, R_L – series resistance, R – recorder, S – cell, V – electrometer, I – picoammeter.

Fig. 1 illustrates the cell and the circuit for the measurement of current–voltage characteristics. The voltage and the current were read with an electrometer (Takeda Riken TR 8651) and a picoammeter (Takeda Riken TR 8641), respectively. A variable resistance between 100 kΩ and 100 MΩ was connected in series with the sample. The samples were examined under an optical and a scanning electron microscope after the switching had occurred. TSC measurements were carried out with the sample which had 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 by use of a thermal program controller (Shinku Riko HPC 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.

3. Results and discussion

3.1. Polystyrene

Fig. 2 shows typical switching current–voltage characteristics. When the applied voltage is low, the sample has a high resistance (this state is called the off-state). When the voltage exceeds the so-called threshold voltage, V_{th}, the current abruptly increases, and a stable low resistance state (the on-state) is formed. The on-state was

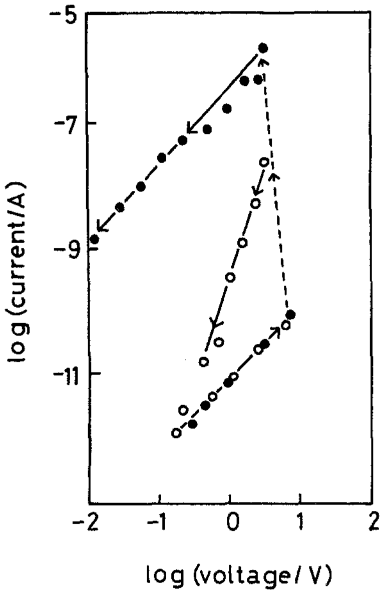

Figure 2 Typical switching characteristics of PST. ● – with 1 MΩ series resistance, ○ – with 100 MΩ series resistance. Film thickness is 0.14 μm.

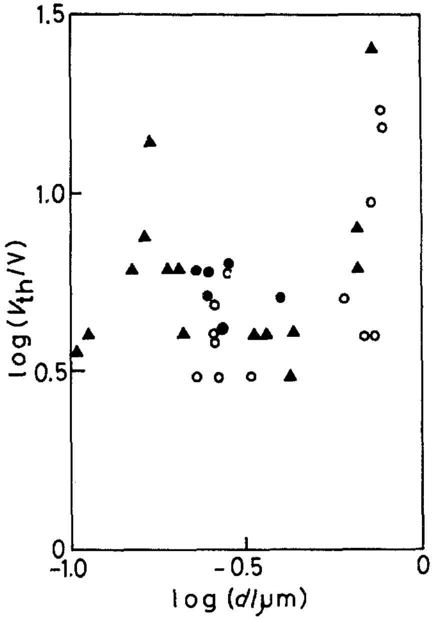

Figure 3 Plot of log V_{th} against log (film thickness). ○ – commercial PST, MW = 2.5 × 10^5, ▲ – catalytically polymerized PST, MW = 2.2 × 10^5, ● – catalytically polymerized PST, MW = 2.6 × 10^4.

memorized when a 1 MΩ series resistance was used; whereas, with a 100 MΩ series resistance, the on-state is unstable and returned to the off-state when the applied voltage was lowered. The memorized on-state in the former case was maintained for more than a month.

Carchano *et al.* [1] observed linearity between the threshold voltage and the film thickness. In the present case, however, for the commercial and the catalytically prepared polystyrene, no distinct relationship was found between V_{th} and the film thickness as shown in Fig. 3. On the other hand, for the polystyrene polymerized by γ-ray irradiation or by heating without any initiators, the threshold voltage increases linearly with the film thickness as indicated in Figs. 4 and 5. These two figures also show that, for the low molecular weight polystyrene, the threshold voltage is higher than that for the high molecular weight polystyrene. The data obtained by Carchano *et al.* [1] were also plotted in Fig. 4. Their polymer has a much higher threshold voltage than those formed by γ-ray initiation. Fig. 4 suggests that the plasma-induced polystyrene is quite different from the γ-ray-induced or thermally polymerized types in electrical properties. In glow discharge polymerization, it has been known that many unsaturated bonds or branches are formed in the polymer. This difference of V_{th} between PST prepared by plasma and that by γ-ray can be explained if a trapping site such as a double bond serves an important role in the switching phenomenon, as in the case of polyvinylcarbazole, in which space charge limited current or Poole–Frankel conduction is related to its switching [5].

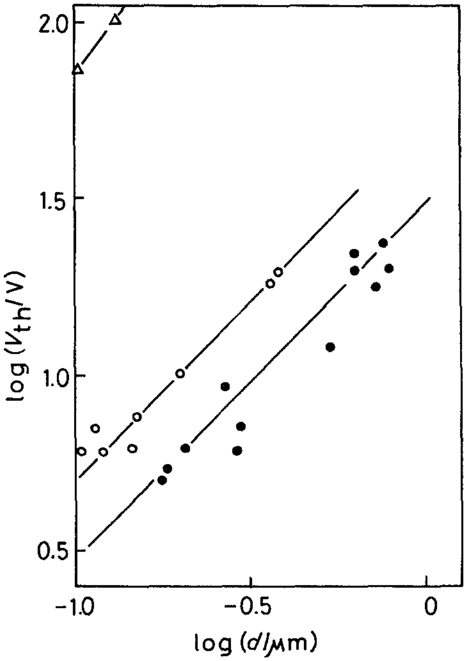

Figure 4 Plot of log V_{th} against log (film thickness) for PST polymerized by γ-irradiation. ○ – MW 5.5 × 10^5, ● – MW 2.2 × 10^6, △ – by Carchano *et al.* [1].

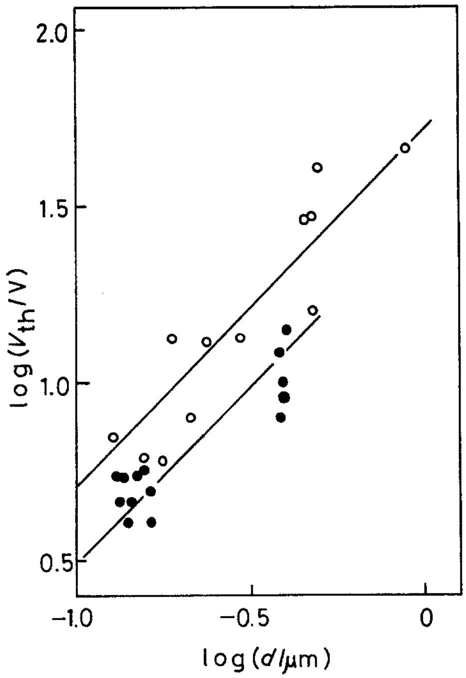

Figure 5 Plot of log V_{th} against log (film thickness) for the thermally polymerized PST. ○ – MW 5.1×10^5, ● – MW 2.7×10^6.

In the previous papers published by Carchano and co-workers [1, 4] Henish and Smith [2], and Pender and Fleming [3], spots or dots were observed through an optical or an electron microscope after the memory switching had taken place. According to their reports, the on-state is due to the metallic filaments formed by the fusion of the metal electrode or the carbon filaments which were formed in the localized pyrolysis of the polymer film. In the present study, these dots or spots were not observed through the SEM after the switching had occurred. However, when a thick film was prepared and high voltage was applied, breakdown occurred without switching. In this case, spots caused by breakdown were observed through a scanning electron microscope, as Carchano *et al.* [1] have reported.

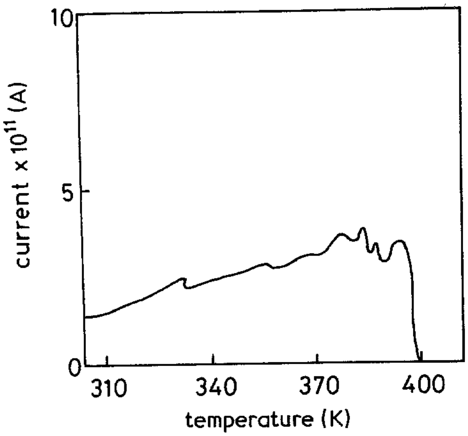

Figure 6 TSC curve for the on-state PST. γ-ray polymerized. MW = 5.5×10^5. TSC was measured at the rate of 10° C cm^{-1} with the field strength 1.1 kV cm^{-1}. The film thickness is 0.90 μm.

TSC measurements were carried out with PST which had been converted to the on-state. The current remained almost constant from 30 to 135° C. Above 135° C, the current became zero indicating that all the trapped charges were released (Fig. 6). This turn-off by heat treatment and turn-on by applying a voltage higher than V_{th} can be repeated many times without any apparent damage.

3.2. Polymethyl methacrylate

Typical switching characteristics are shown in Fig. 7. The effect of the series resistance on the type of switching is similar to that for polystyrene. In the case of memory switching, the on-state gradually changes to the off-state. The duration of the on-state is shorter than in the case of PST. Fig. 8 illustrates the switching characteristics observed after several days after the sample had converted to the on-state. The on-state did not

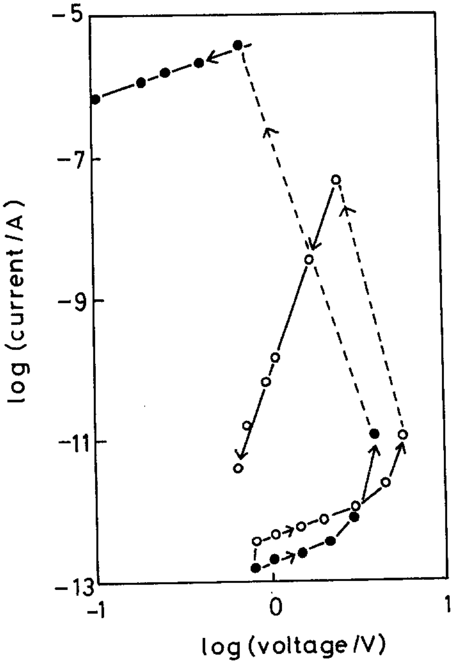

Figure 7 Typical switching characteristics of PMMA. ● – with 1 MΩ series resistance, ○ – with 100 MΩ series resistance. Film thickness is 0.024 μm.

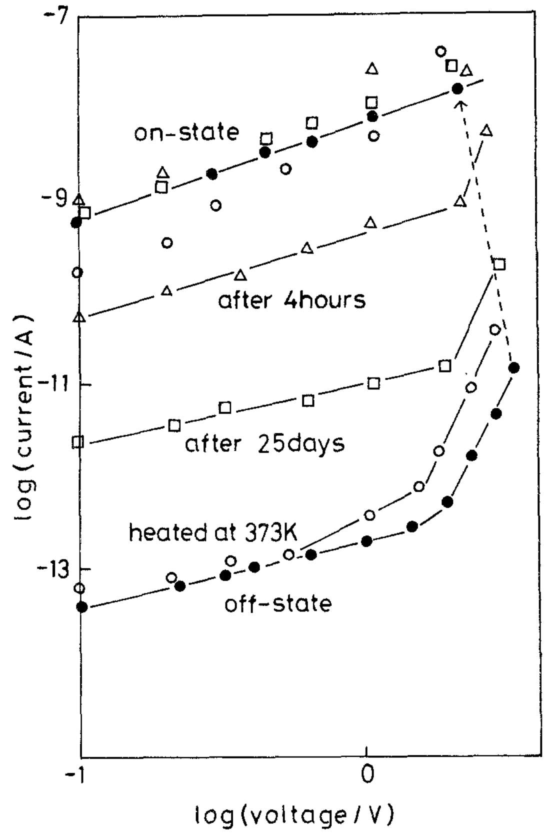

Figure 8 Stability of the on-state of PMMA. Thermally polymerized. MW = 1.1 × 10^7. Film thickness is 0.031 µm.

return completely to the off-state even after 25 days. However, when the sample was heated to 373 K, the off-state was completely recovered. Switching characteristics similar to that in the first run were observed with this heat treated sample as shown in this figure. In the case of PMMA, the molecular weight dependence of the threshold voltage is not so clear as in the case of PST. Fig. 9 shows a plot of V_{th} against the film thickness, both on a logarithmic scale with three different PMMA samples, that is, PMMA polymerized by γ-ray irradiation, by catalytic polymerization with AIBN, and by thermal polymerization without a catalyst. All three polymers have nearly the same molecular weight. The result indicates that, in contrast to the case with PST, in the case of PMMA the conditions or the methods of polymerization do not affect the switching characteristics.

On the contrary, in the case of polystyrene the degree on scatter in a V_{th} against thickness plot depends on the conditions of polymerization. The differences in scatter in this plot between PST and PMMA may be due to the difference in the ease of purification through repeated precipitation.

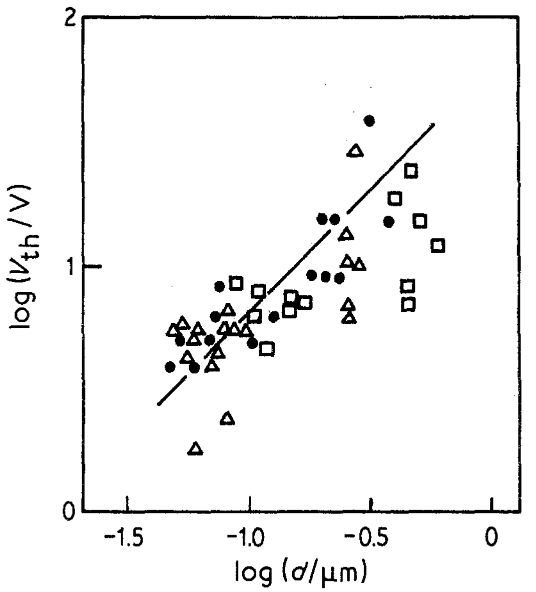

Figure 9 Effect of polymerization conditions on switching characteristics of PMMA. □ – catalytically, MW = 6.5 × 10^5. △ – with γ-irradiation, MW = 7.1 × 10^5. ● – thermally, MW = 2.8 × 10^6.

The TSC curve is shown in Fig. 10. The on-state changes to the off-state at 130° C.

4. Conclusions

Switching without any sort of break in the sample has been successful when a high resitance was connected in series with the sample. In the case of PST, the higher the molecular weight, the lower

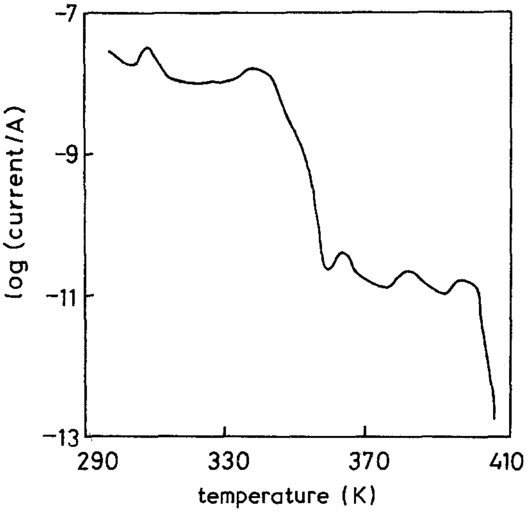

Figure 10 TSC curve for the on-state PMMA. Thermally polymerized. MW = 1.1 × 10^7.

was the threshold voltage. It seems that the chain ends play an important role in switching, for example, a sort of trapping site. The impurities which cannot be eliminated during purification affect the results significantly. In the case of PMMA, neither the procedure of polymerization nor the molecular weight affects the switching characteristics. In PMMA the polymer ends do not seem to constitute traps. In both polymers, switching must be caused by some electronic mechanism, because no traces of breakdown were observed through a scanning electron microscope. In addition, the off-state was recovered by heat treatment of the sample which had been switched on.

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