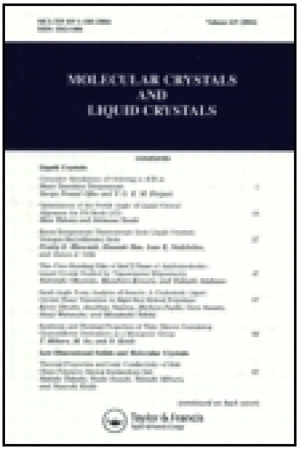

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Characterisation and Application of Carbazole Modified Polysiloxanes in Electrochemical Displays

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CHARACTERISATION AND APPLICATION OF CARBAZOLE MODIFIED POLYSILOXANES IN ELECTROCHEMICAL DISPLAYS

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Abstract Carbazole Modified Polysiloxanes have been cross-linked to form electrochromic thin films. Composite materials containing a variety of counter-ions have been found to undergo reversible switching between a colourless (reduced) and green (oxidised) state, with the reproducibility being determined by the growth rate and the nature of the counter-ion. Investigations in a two terminal transmitting cell structure reveal the density of dicarbazolyl moieties to be ~ 10^{21}cm^{-3}. The rate limiting step in the colouration process appears to be ion transfer across the electrolyte-film interface, whereas bleaching appears to be controlled by a double extraction mechanism. Films containing different spacer groups possess similar colouration times, while bleaching rates vary significantly.

INTRODUCTION

Polysiloxanes with pendant carbazole groups have been shown[1] to undergo electrochemical cross-linking to give electrochromic materials which are transparent in the reduced state and dark green in the oxidised state. This colour change is similar to that obtained for cross-linked PVK[2], where the relative rigidity of the polymeric backbone leads to comparatively poor cross-linking efficiencies and therefore to low densities of colouration centres. The enhanced flexibility of the system under study which results both from the flexible backbone and the pendant nature of the active groups is expected to result in an enhanced performance.

EXPERIMENTAL DETAILS

Carbazole modified polysiloxanes (CMPS) were prepared by platinum catalysed hydrosilylation reactions between polymethylhydrosiloxane (Petrarch, MW = 2250, n = 35, MW = 5105, n=80) and carbazol-9-ylalk-1-enes (m = 3 or 11) as previously reported[1,3]. Cross-linking of the polymers was performed in air using a standard three terminal electrochemical cell and a constant current technique. The working electrode was a glass substrate patterned with gold on chromium, while the counter electrode was aluminium and a silver reference electrode was employed. Thin films were deposited from 0.1M electrolytic solutions of tetrabutylammonium hexafluorophosphate in dried dichloromethane and CMPS (0.5 mg cm^{-3}). Cell current densities were varied from 4 - 500 $\mu A\ cm^{-2}$, while growth times were in the range 72-9000 seconds. Film deposition rates were $\approx$ 50Å s^{-1} $(\mu A/cm^2)^{-1}$ for cell current densities of 10 - 100 $\mu A\ cm^{-2}$.

Step response characteristics (figure 1) were obtained within a two terminal cell, using fast sample-and-hold (s/h) logic, with the current transients for colouration and bleaching being recorded on a digital oscilloscope. The amount of charge Q_s transferred between the coloured and bleached states was estimated by temporal integration of the bleaching current J_b. Time-resolved electro-optic response measurements were performed using a red LED (640nm) and fast pin-photodiode combination aligned through the cell. The spectral properties of the films in various colouration states were alternatively measured in air using a commercially available UV-vis spectrophotometer.

Lifetime measurements were conducted by monitoring the cyclic voltammograms, during repeated cycling in a 0.1M electrolytic solution containing the relevant salt, of films prepared using different current densities and electrolytes.

RESULTS AND DISCUSSION.

Static Response

An important parameter in determining the potential applicability of an electrochromic material is the change in optical density δOD, defined as the ratio of transmitted light in the coloured state (T_c) to that in the bleached state (T_b) according to $\delta OD = \log(T_c/T_b)$. Spectral curves (figure 2), at different colouration potentials V_c, were obtained for a 0.8 μm thick cross-linked (XL) film where the colouration time t_c was 300 seconds (a satisfactory colour change is observed after one second). It is evident that the oxidised films are optically dense in both the blue and the red regions of the visible spectrum rendering the state characteristically green in colour. The degree of colouration, defined by the contrast ratio $CR = OD^{-1}$, increases with V_c and is accompanied by an increase in Q_s as demonstrated for three films of different thickness l (figure 3). For $V_c \geqq 2.0V$, Q_s increases exponentially with V_c with the rate of increase being independent of l. The origin of this lies in the dynamics of the colouration and bleaching processes. The density θ of coloured dicarbazolyl centres at a given V_c may be estimated[4] from the amount of transferred charge Q_s as $\theta = \Phi Q_s/2el$ where Φ is the colouration

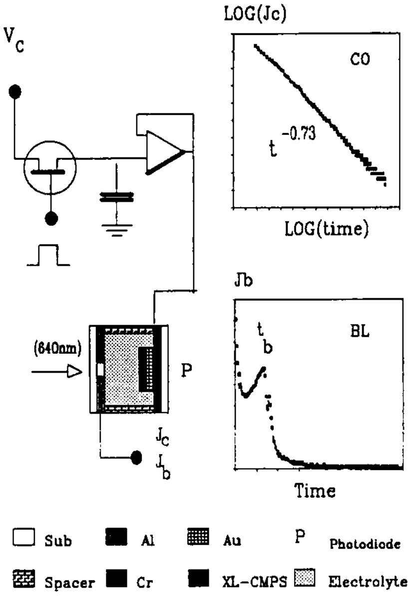

FIGURE 1 Experimental arrangement of transmitting cell and s/h logic. Insets show typical colouration (CO) and bleaching (BL) current transients.

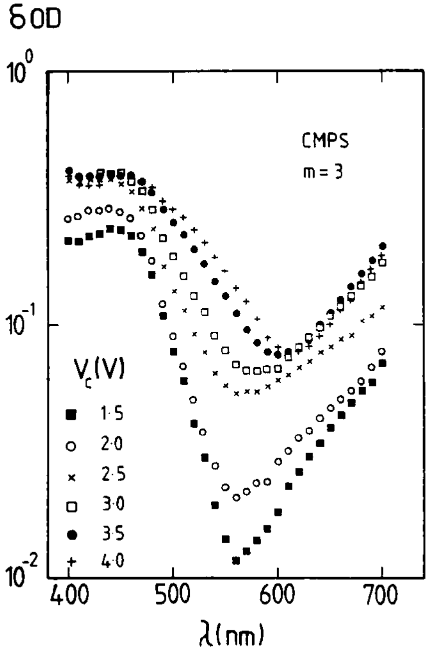

FIGURE 2 Spectral response of δOD for various V_c. l=0.8μm.

efficiency. The factor of 2 in the denominator reflects the number of electronic charges required per colouration centre. Prior measurements[1] suggest $\Phi = 25\%$ which, from the data of figure 3, renders 1.5×10^{20} cm^{-3} $< \theta <$ 2×10^{21} cm^{-3} for $2.0V < V_c < 3.5V$, in good agreement with the value calculated from the material molecular weight of 1.2×10^{21}cm^{-3}. However, a reliable estimate of the maximum θ value is complicated by the possible onset of further oxidation processes at higher V_c.

A linear dependence of δOD on Q_s is expected[4] for electrochromic systems in which a product is deposited onto the working electrode during colouration. Such behaviour is shown in figure 4 for two colouration potentials where δOD and Q_s have been evaluated during a bleaching cycle. This indicates that the mass adsorption coefficient depends directly upon the fraction of colouration centres which are 'active'.

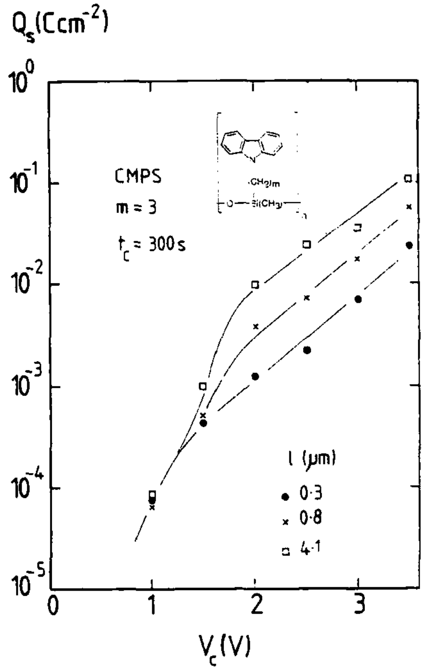

FIGURE 3 Variation of Q_s with V_c for films of thickness l. Fully coloured states ($Q_s = Q_m$) are achieved for t_c=300s

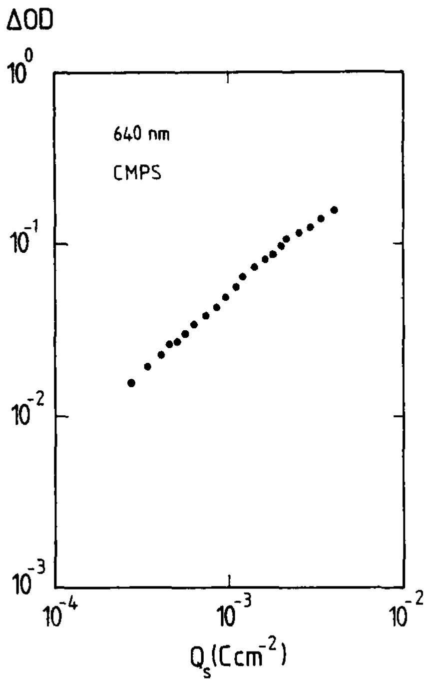

FIGURE 4 Linear variation of δOD with Q_s. l = 0.8μm.

Dynamic Response

Colouration.

The time resolved response of an electrochromic material may be used to identify the physical and chemical processes responsible for the redox reactions. During colouration (figure 5), Q_s is found to depend upon V_c and to saturate as $t_c \rightarrow \infty$, with the saturation value Q_m dependent on V_c as previously noted in figure 3. Assuming that the rate limiting process in the colouration step is ionic transfer across the electrolyte-film interface, it may be shown[5] that for a double-layer barrier having a symmetry factor α, the ionic current density, j_i, is given by

$$j_i = j_o\{\exp[(1-\alpha)e\Gamma/kT] - \exp[-\alpha e\Gamma/kT]\} \qquad (1)$$

where j_o is the exchange current density, Γ is the potential drop across the interface when $j_i \neq 0$ and all other symbols have their usual meanings. Given that $Q_s \rightarrow Q_m$ as $t_c \rightarrow \infty$ then Γ must become vanishingly small (since $j_i \rightarrow 0$). If the chemical potential η of the material depends upon Q_s, a self-limiting mechanism is then provided since $\Gamma = V_c - \eta(Q_s)/eN_A$, where N_A is Avogadro's number. This concept has been successfully applied to the colouration process observed in amorphous WO_x film[6]. Since $Q_s(t_c)$ depends upon the temporal variation of j_i, then $Q_s(t_c)$ is driven by changes in η whose functional form consists of an entropic contribution due to the distribution of holes and PF_6^- ions in the film, together with a free energy contribution arising from the concomitant increase in lattice energy. Assuming this latter component to be dominant, then it is expected that the oxidised films will possess a built-in potential V_{bi} equal to V_c if $t_c \rightarrow \infty$.

The explicit dependence of V_{bi} and hence η upon Q_s can be determined from the bleaching currents at a given V_c, with the effective bleaching potential given by $V_b^* = V_{bi} - V_b$, where V_b is the externally applied bleaching voltage. Assuming that the bleaching currents are space charge limited and due to the flow of both negative ions and positive holes from an initially neutral system, it is possible to show[7]

$$t_b = Q_s l^3/4\varepsilon_r\varepsilon_o\mu_i(V_b^*)^2 \tag{2}$$

where μ_i is the ionic mobility and ε_o and ε_r are the permittivity and relatively permittivity of free space and the film respectively. Figure 6 shows that the XL-CMPS data obey this equation with the bleaching times, t_b, identified from the cusp of the bleaching current (figure 1). By extrapolating the curves to $\sqrt{(1/t_b)} = 0$, V_{bi} is obtained from the intercept on the V_b axis. The relationship between Q_s and V_{bi} (inset figure 6) is then found to take the empirical form $V_{bi} = V_{bi}^o \ln(Q_s/Q_o)$ with $V_{bi}^o = 0.6V$ and $Q_o = 0.05$ mC cm^{-2} and consequently it is found that $\Gamma = -V_{bi}^o \ln x$ and $j_i = j_o[x^{-(1-\alpha)\delta} - x^{\alpha\delta}]$, where $x = (Q_s/Q_m)$ and $\delta = eV_{bi}^o/kT$. Charge conservation between the electrolyte and the film requires that $dx/dt = j_i/e\theta l$ and hence

$$\int[x^{-(1-\alpha)\delta} - x^{\alpha\delta}]^{-1}dx = t_c/\tau_o \tag{3}$$

where $\tau_o = e\theta l/j_o$. This cannot be solved to give an explicit functional dependence of x upon t_c. However, for the present case of $V_{bi}^o = 0.6V$, a measurement temperature of 300K and if the colouration times are restricted such that Q_s is small, the second term in the integrand may be ignored and

$$[Q_s/Q_m]^{(23-22\alpha)} \approx (23-22\alpha)[t_c/\tau_o] \tag{4}$$

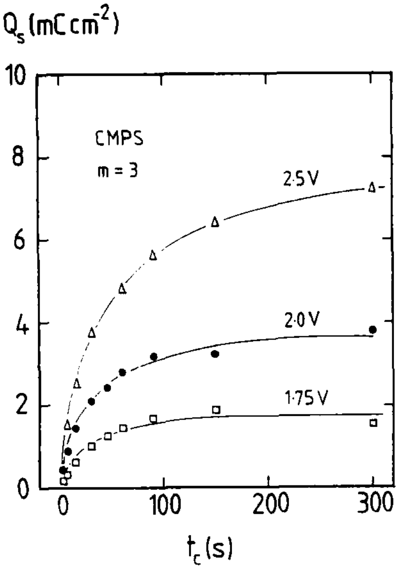

FIGURE 5 Dynamics of colouration showing Q_s as a function of t_c for various V_c. $l = 0.8\mu m$.

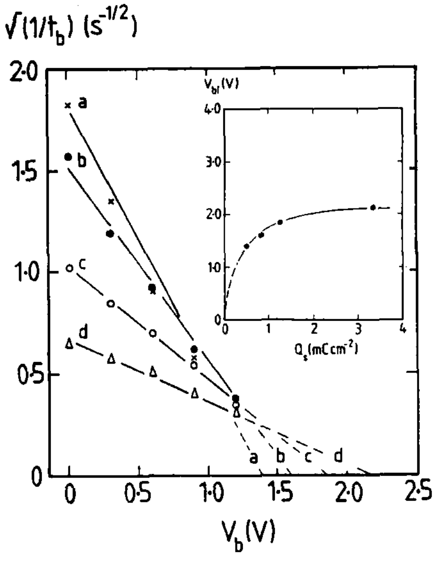

FIGURE 6 Dynamics of bleaching showing $1/t_b$ vs V_b. Inset shows dependence of V_{bi} on Q_s. $l = 0.8\mu m$.

This results in a best fit to figure 5 for $\tau_o \approx 600s$ and $\alpha \approx 0.9$, indicating a highly asymmetric barrier at the electrolyte-film interface[5].

For $\alpha \approx 0.9$, the colouration current density at short times is expected to vary as $j_i \approx j_o(t_c/\tau_o)^{-0.69}$ in reasonable agreement with the experimental current decay data shown in figure 1. Taking $\theta \approx 10^{20}$ cm^{-3}, the fitted value of τ_o implies an exchange current density $j_o \approx 2$ μA cm^{-2}. Thus the observed empirical relationship between V_{bi} and Q_s can be used to explain both the colouration dynamics and the exponential dependence of Q_s on V_c, since at saturation $\Gamma = 0$ and $V_c = V_{bi}^o \ln(Q_m/Q_o)$. By analysis of the data of figure 3 it is found that $V_{bi}^o = 0.56V$, similar to the value obtained above.

Bleaching.

The space charge limited current theory utilised to obtain equation 2 predicts that the bleaching currents should decay in a single power law fashion without exhibiting any of the structure observed experimentally. The 'cusp' is more characteristic of transient space charge limited behaviour[8]. However, if this were the case then t_b would be expected to vary as $(V_b^*)^{-1}$ and have little dependence on Q_s. Such predictions are

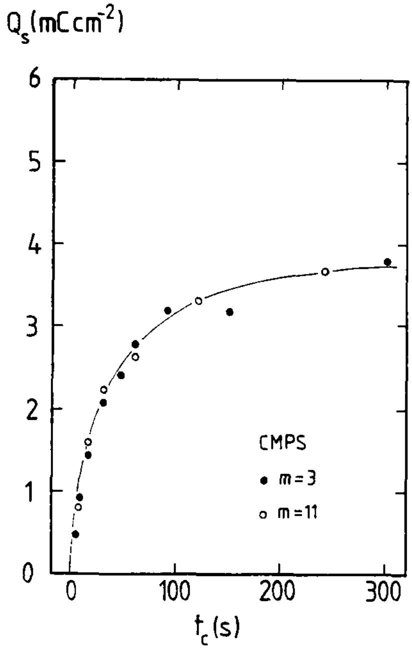

FIGURE 7 Comparison of colouration rates for m=3 and m=11 XL-CMPS. V_c = 2.0V, l = 0.8μm.

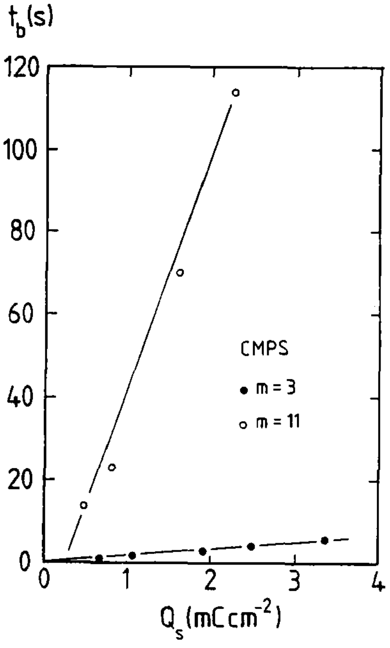

FIGURE 8 Comparison of bleaching rates for m=3 and m=11 XL-CMPS. V_c = 2.0V, l = 0.8μm.

clearly at variance with the experimental data (figures 6 and 8). Therefore, while it would appear that the identification of the bleaching time with the 'cusp' feature is correct, the origin of this 'cusp' remains unclear.

It is possible to obtain μ_i within the electrochromic film from equation 2 using the data of figure 6, if it is assumed that the hole mobility is significantly higher than the ionic mobility. Assuming $\varepsilon_r \approx 3$, $\mu_i \approx 2\times10^{-4}\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ for the PF_6^- counter-ions in the m=3 material.

Influence of Spacer Length

Electro-optical measurements on m=3 and m=11 materials are essentially identical as are the colouration dynamics (figure 7). This implies that the density of colouration centres in both cases is similar and provides supporting evidence for the rate-limiting process in the colouration step being ionic transfer across the electrolyte-film interface. Interestingly the bleaching rates are very different (figure 8), with the m=11 material significantly slower. The ionic mobility for the m=11 material is $\approx 10^{-6}\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$, a factor of 200 smaller than for the m=3 material. It is tentatively proposed that this may be due to enhanced space filling between the dicarbazolyl groups by the additional methylene spacers in the m=11 polymer.

Lifetime

Measurements have been conducted on films grown at different rates and incorporating different counter-ions (PF_6^-, ClO_4^- and BF_4^-). Films grown at the highest growth rates display a matt finish due to the existence of large numbers of particulates, while those grown more slowly display an extemely bright finish. Cyclic voltammograms (50mV/s) reveal smaller peak heights and therefore lower colouration densities in the more particulate films. Lifetime tests show that these films display no visible colour change after ~ 20-100 cycles. Films prepared at the lowest growth rates last longest with visible colour changes being observed for > 1000 cycles. Variation of the counter-ion is found not to significantly influence the peak heights (and hence θ) of the cyclic voltammograms or the number of particulates formed for the different growth rates. However, there is preliminary evidence to suggest that the different counter-ions may influence the lifetime by up to a factor of 5, with films containing PF_6^- counter-ions surviving longest.

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