

Electroactive carbazole-substituted polysiloxanes

B. Tieke and M. O. Chard

Ciba-Geigy AG, Research Center, CH-1701, Fribourg, Switzerland

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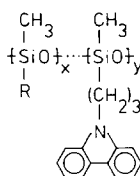
Polysiloxane homo- and copolymers with various carbazole concentrations in the substituents were prepared and their electroactive properties studied by cyclic voltammetry and optical absorption spectroscopy. Electrochemical oxidation leads to dimerization of the carbazole units, which thereby crosslinks the polymer. The oxidized films exhibit conductivities up to $8 \times 10^{-4} \text{ S cm}^{-1}$. Depending on the potential applied, the films are either deep blue, pale green or colourless. The electrochromism is excellently reversible. The chemical processes involved in electrochemical oxidation and cycling of the polymers are discussed in detail.

(Keywords: carbazole; polysiloxane; electrochromism; electrical conductivity)

INTRODUCTION

Electroactive polymer films are of great interest because of potential applications, e.g. as conductive coatings or electrochromic displays. As part of our studies on novel electroactive materials, we investigated a number of carbazole-substituted polysiloxane homo- and copolymers (Cz-PSi). Our interest in these polymers was stimulated by recent publications on electroactive properties of carbazole-containing polymers, e.g. poly(*N*-vinylcarbazole)^{1,2} or poly(2-*N*-carbazolyethyl vinyl ether)³, which made it worth while to study the electrochemical behaviour of Cz-PSi, too. While carbazole-containing homopolysiloxanes have been described already⁴, no information is available on corresponding copolymers with variable carbazole concentrations. Thus, additional interest in Cz-PSi arose from the effect of copolymer formation on the properties of the polymers.

In the present study we report on synthesis, electroactive and thermal properties of carbazole-substituted polysiloxane homo- and copolymers of the common formula:



with R being CH_3 or $\text{n-C}_8\text{H}_{17}$, and x and y referring to the copolymer composition described in detail below. Studies on the electroactive properties were carried out by cyclic voltammetry and optical absorption spectroscopy. Furthermore, conductivity measurements of the electrochemically oxidized polymers are reported and the effects of the carbazole concentration on the electroactive properties are described.

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EXPERIMENTAL

Materials

Cz-PSi were synthesized according to a procedure described for the homopolymer⁴ by reacting *N*-allylcarbazole⁵ with poly(methylhydrosiloxane), poly(methylhydrosiloxane-*co*-dimethylsiloxane) and poly(methylhydrosiloxane-*co*-methyl-*n*-octylsiloxane), all purchased from Petrarch.

Electrochemical oxidation

Electrochemical oxidation of the polymers was carried out in a 500 ml glass vessel equipped with two platinum electrodes ($50 \times 20 \times 1 \text{ mm}$) and an Ag/AgCl reference electrode. Both 'film electrolysis' and 'solution electrolysis' were applied.

For 'film electrolysis' the platinum anode was coated with a thin film of the Cz-PSi (thickness $\leq 1 \mu\text{m}$) and immersed in an electrolyte solution containing a non-solvent of the polymer (e.g. acetonitrile, propylene carbonate) and a supporting electrolyte (tetrabutylammonium hexafluorophosphate, Bu_4NPF_6 , at concentrations of 0.02 to 0.2 mol l^{-1}). Prior to film electrolysis the solution was purged with argon for 30 min. Upon current flow the polymer film rapidly turned green, indicating that the oxidation process was occurring.

For 'solution electrolysis' a 0.01 M polymer solution in dichloromethane was prepared containing a supporting electrolyte at a concentration of 0.02 to 0.1 mol l^{-1} . The polymer solution was purged with argon and subsequently subjected to electrolysis. The anode turned rapidly green indicating the deposition of oxidized polymer. Details of the electrolysis are given later in Table 2. All experiments were carried out under extreme protection against air and moisture.

Conductivity

Conductivity measurements were carried out on electrochemically oxidized polymers. The polymers were pressed into pellets and measured at room temperature using a two-probe technique.

Cyclic voltammetry

Cyclic voltammetric studies were carried out using an AMEL potentiostat (model 552) equipped with a digital integrator (model 731) and function generator (model 567). Measurements were performed at room temperature in a 50 ml glass cell equipped with argon bubbler, two platinum electrodes (surface area 50 mm²) and an Ag/AgCl reference electrode. Films investigated were deposited on the electrode either by casting from solution or by 'solution electrolysis' as described above.

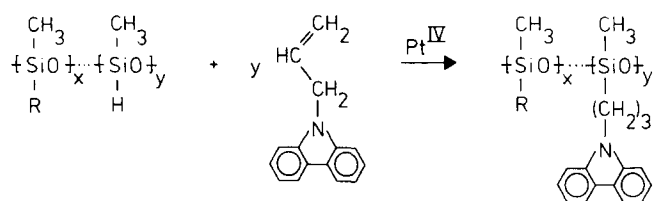
Optical absorption

Optical absorption spectra were recorded on Perkin-Elmer spectrometers Lambda 7 and Lambda 9 using a test cell which consisted of two ITO (indium tin oxide) coated glass plates (40 × 40 × 1 mm) separated by a 10 mm Teflon spacer. For the spectroelectrochemical study a thin transparent polymer film was deposited on the electrode by 'solution electrolysis' as described above. In all experiments the test cell contained a 0.01 M solution of Bu₄NClO₄ in dry dichloromethane saturated with argon.

RESULTS AND DISCUSSION

Starting materials

Cz-PSi were synthesized according to Scheme 1:



Scheme 1 Polymer synthesis

Some of their characteristic properties are listed in Table 1. As shown by the table, the glass temperature of the polymer is lowered when the concentration of

Table 1 List of carbazole-substituted polysiloxanes and some of their characteristic properties

| Polymer no. | Composition | | | <i>T_g</i> (°C) | Yield ^a (% of theory) | Weight-average molecular weight ^b |
|-------------|----------------------------------|------|------|---------------------------|----------------------------------|--|
| | R | x | y | | | |
| 1 | CH ₃ | 0 | 1 | 51 | 78 | 71 000 |
| 2 | CH ₃ | 0.5 | 0.5 | 15 | 77 | 3 000 |
| 3 | CH ₃ | 0.83 | 0.17 | -40 | 54 | 5 800 |
| 4 | n-C ₈ H ₁₇ | 0.53 | 0.47 | -20 | 89 | 61 000 |

^a Amount of polymer recovered

^b Determined by gel permeation chromatography in tetrahydrofuran

Table 2 List of preparation conditions and specific conductivities of electrochemically oxidized polymers 1-4

| Starting polymer | Method | Solvent | Supporting electrolyte ^a | Yield ^b (mg) | Current density (mA cm ⁻²) | σ (S cm ⁻¹) |
|------------------|--------|---------------------------------|-------------------------------------|-------------------------|--|--------------------------------|
| 1 | A | CH ₂ Cl ₂ | Bu ₄ NBF ₄ | 123 | 1 | 3.3 × 10 ⁻⁴ |
| 1 | A | CH ₂ Cl ₂ | Bu ₄ NPF ₆ | 85 | 1 | 3.4 × 10 ⁻⁴ |
| 1 | A | CH ₂ Cl ₂ | Bu ₄ NClO ₄ | 162 | 1 | 8.3 × 10 ⁻⁴ |
| 2 | A | CH ₂ Cl ₂ | Bu ₄ NClO ₄ | 21 | 1 | 1.6 × 10 ⁻⁴ |
| 3 | A | CH ₂ Cl ₂ | Bu ₄ NClO ₄ | 14 | 0.5 | 1.7 × 10 ⁻⁶ |
| 4 | A | CH ₂ Cl ₂ | Bu ₄ NClO ₄ | 28 | 0.5 | 2.5 × 10 ⁻⁵ |
| 1 | B | Propylene carbonate | Bu ₄ NPF ₆ | | 1 | 4.7 × 10 ⁻⁹ |

^a Concentration: 0.1 mol l⁻¹

^b Weight of anodic deposit after 1 h electrolysis

dimethylsiloxane comonomer units is increased. Obviously the comonomer acts as an intramolecular plasticizer. The effect is even more pronounced when methyl-n-octylsiloxane units are present in the copolymer. All polymers were obtained in good yields except for 3, which is a liquid and can hardly be separated from the reaction mixture. The molecular weights essentially correspond to those of the starting polymers and indicate that no or only very little crosslinking has taken place.

Electrical conductivity of oxidized films

The starting polymers 1-4 were oxidized by solution electrolysis (method A) and by film electrolysis (method B). Preparation conditions and specific conductivities are listed in Table 2. Oxidized films prepared according to method A always showed much higher conductivities than those prepared by method B. This is caused by the poor swelling of the polymer films in propylene carbonate or acetonitrile, rendering the diffusion of counterions into the polymer very difficult. Conductivities up to nearly 10⁻³ S cm⁻¹ were measured for films deposited on the platinum anode from a solution containing polymer 1 in CH₂Cl₂/0.1 M Bu₄NClO₄. The oxidized polymers were excellently stable in argon atmosphere but very unstable in air. Under ambient conditions they decomposed within a few hours and the conductivity dropped by 2-3 orders of magnitude.

Cyclic voltammetry

A cyclic voltammogram of a thin film of polymer 1 coated on a platinum electrode is shown in Figure 1. During the first scan only a single anodic wave at about 1.3 V vs. Ag/AgCl occurs. On reversing the scan at 1.4 V and cycling back a shoulder appears at 1.2 V followed by a cathodic peak at 1.0 V. All subsequent scans show two anodic (1.1 and 1.3 V) and two cathodic waves (1.2 and 1.0 V). While the anodic and cathodic waves at the higher potentials can be ascribed to oxidation and reduction of carbazole units, the two additional waves at lower

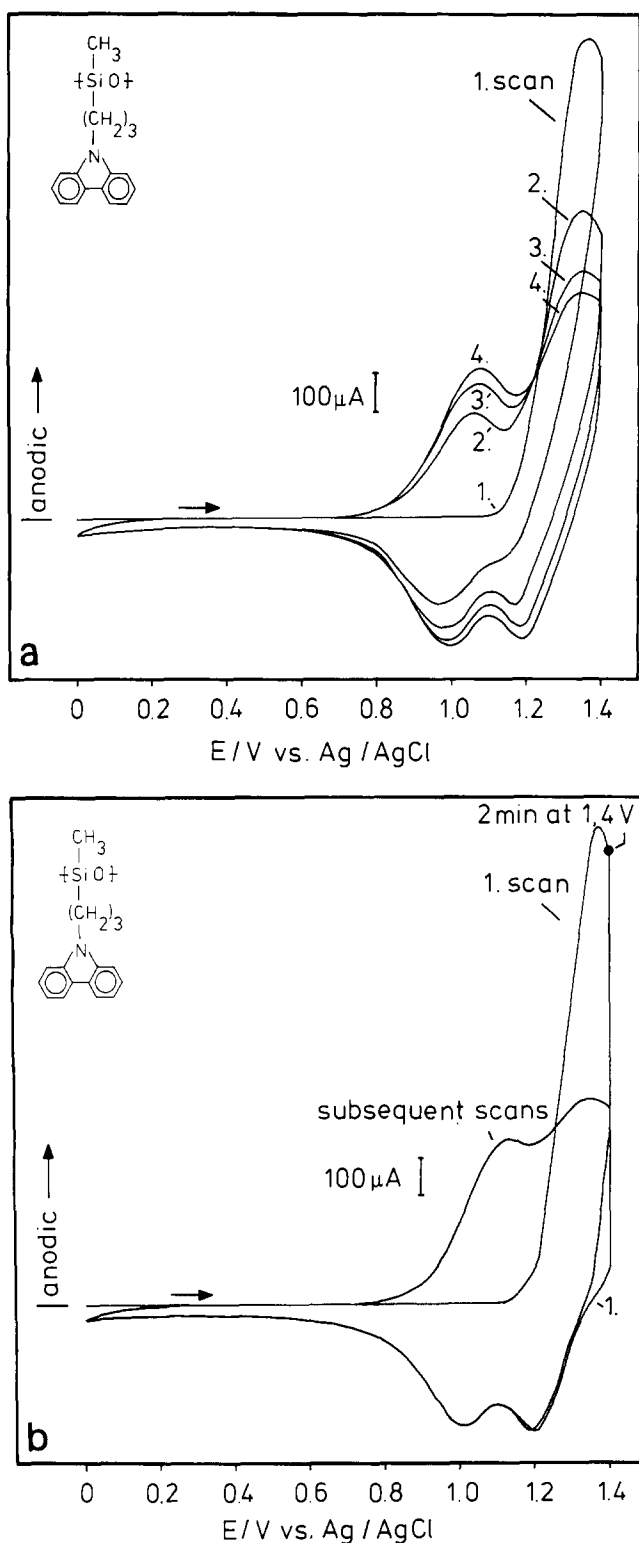


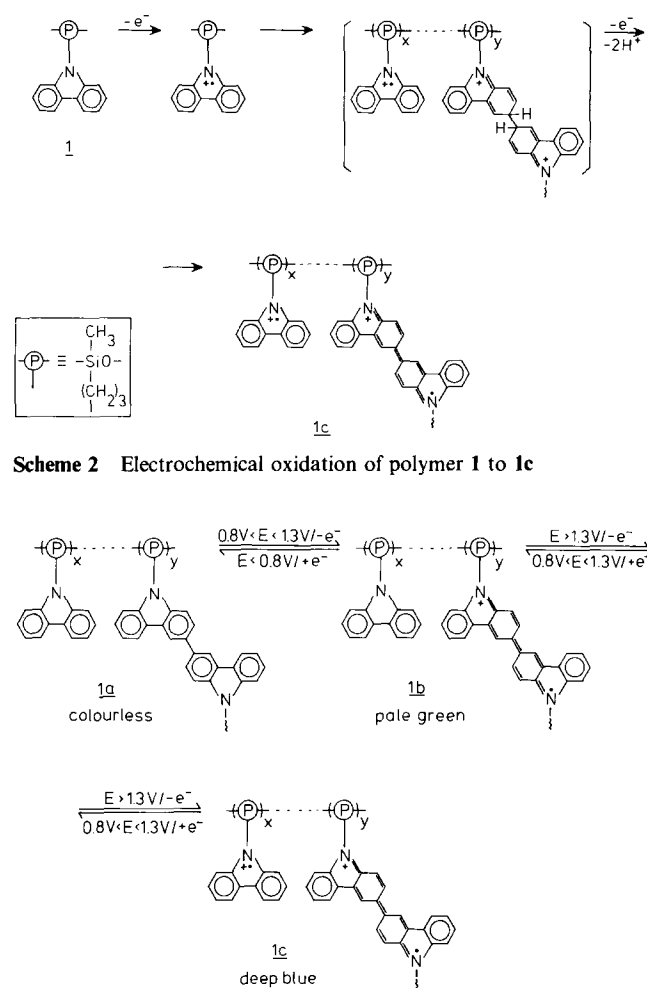
Figure 1 Repetitive cyclic voltammograms of thin films of polymer **1** coated on a platinum electrode. Solvent: $\text{CH}_3\text{CN}/0.1 \text{ M Bu}_4\text{NClO}_4$. (a) Continuous scan and (b) first scan stopped at $E = 1.4 \text{ V}$ for 2 min. Scan rate: 20 mV s^{-1}

potentials originate from a second redox-active species, the 3,3'-dicarbazolyl unit, which is formed by dimerization of the carbazole cation radicals⁶. Since the dimer oxidation potential is lower than that of the monomer carbazole unit, the dimers are immediately oxidized under the potential applied.

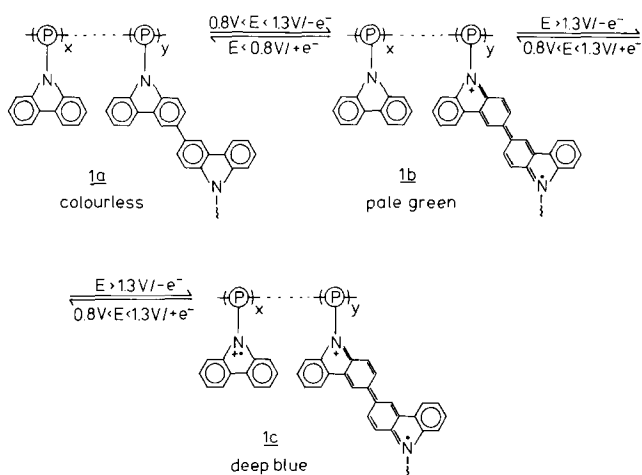
During successive cycling the anodic wave of the 3,3'-dicarbazolyl unit increases gradually in intensity, while

the wave of the carbazole unit decreases (Figure 1a). This indicates the occurrence of dimerization, which is obviously not completed during a single voltammetric cycle. The situation is completely different, however, when the first scan is interrupted at a potential of 1.4 V for a period of 2 min and then continued. As Figure 1b shows, all subsequent scans are now identical in shape. This demonstrates that dimerization has gone to completion and that no other side-reaction has taken place. Up to a potential of 1.4 V the electrochemical cycling of Cz-PSi is completely reversible. The scans in Figure 1b also show that part of the carbazole units remains unreacted presumably because they attain a position sterically unfavourable for dimerization.

The chemical reactions involved in the electrochemical oxidation and cycling of polymer **1** are outlined in Schemes 2 and 3:



Scheme 2 Electrochemical oxidation of polymer **1** to **1c**



Scheme 3 Reversible electrochemical cycling between polymers **1a**, **1b** and **1c**

In the initial step the carbazole units are oxidized and cation radicals are formed. The cation radicals dimerize irreversibly and the 3,3'-dicarbazolyl units thus formed are immediately oxidized under the reaction conditions applied (Scheme 2). Hence, a fully oxidized polymer **1c** is obtained. Depending on the potential applied, polymer **1c** can be reduced to polymers **1b** or **1a** containing oxidized 3,3'-dicarbazolyl units and neutral carbazole units or only neutral species. The formation of the individual redox states is completely reversible (Scheme 3). Polymers **2-4** behave analogously.

In Table 3 the anodic peak potentials of electrochemical deposits of polymers 1–3 are listed. Increasing carbazole concentration of the polymer causes a shift of the first anodic wave to a higher potential. The change in oxidation potential may originate from charge-transfer interactions presumably between adjacent dimer units or dimer and monomer units, as discussed more in detail in the following section. Its extent is clearly dependent on the respective carbazole concentration of the polymer.

Optical absorption spectroscopy

In Figure 2 optical absorption spectra are shown originating from an electrochemically deposited film of polymer 1 on ITO glass. Spectra were recorded while different potentials were applied to the film. In general, three different types of spectra were observed. At zero potential the film composition corresponds to polymer 1a in Scheme 3. Only neutral carbazole and 3,3'-dicarbazolyl units are present and the film is colourless. For comparison, the solution spectrum of polymer 1 included in Figure 2 shows that the polymer absorbs in the ultra-violet only. Applying a potential of $E = 1.0$ V vs. Ag/AgCl changes the polymer composition to 1b (Scheme 3). The formation of the 3,3'-dicarbazolyl cation radicals is indicated by the pale green colour of the film with absorption maxima at 390 and 890 nm. Applying a potential of $E \geq 1.3$ V causes the residual carbazole units to become oxidized, too. The formation of the carbazole cation radicals is indicated by a deep blue colour of the film. The absorption maximum is at about 720 nm. In an argon atmosphere the colour changes are completely reversible, whereas under ambient conditions a gradual decomposition takes place.

As shown by Figure 3, the 3,3'-dicarbazolyl cation radicals exhibit a broad near-infra-red absorption with a shoulder at about $1.25 \mu\text{m}$. The intensity of this shoulder relative to the 890 nm absorption is strongest for polymer 1 with the highest carbazole concentration. The near-infra-red absorption can be ascribed to a charge-transfer interaction between oxidized 3,3'-dicarbazolyl units and presumably neutral dimer or monomer carbazole units. Similar observations were made recently⁷ by studying the chemical oxidation of poly(*N*-vinylcarbazole) with SbCl_5 .

SUMMARY AND CONCLUSIONS

Our investigations show that Cz-PSi can be oxidized electrochemically with the formation of deeply coloured films and $\sigma \leq 8 \times 10^{-4} \text{ S cm}^{-1}$. Oxidation of the polymers leads primarily to carbazole cation radicals, which partly dimerize and thereby crosslink the polymer. Depending on the potential applied the crosslinked films are either colourless (neutral state), pale green (3,3'-dicarbazolyl

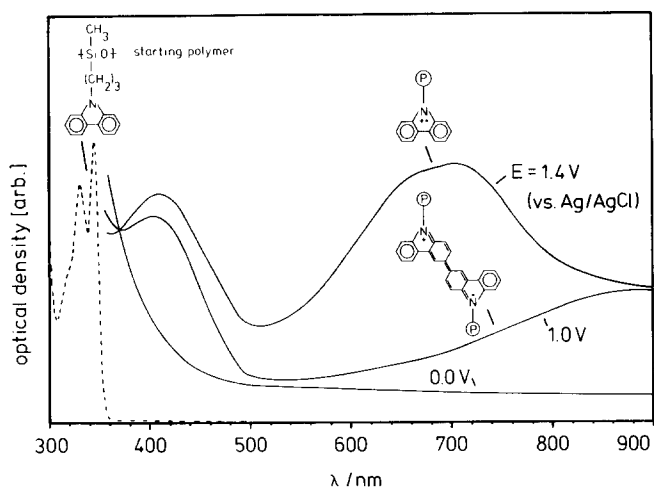


Figure 2 Absorption spectra of an electrochemically deposited film of polymer 1 on ITO glass. Spectra were recorded while different potentials were applied to the film. For comparison, a solution spectrum of polymer 1 in dichloromethane is also shown (---)

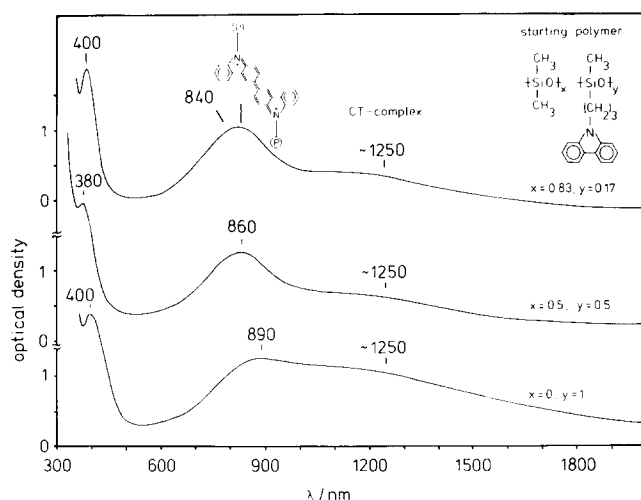


Figure 3 Absorption spectra of electrochemically deposited films of polymer 1–3 on ITO glass. Spectra were recorded while a potential of 1.1 V (vs. Ag/AgCl) was applied to the films

cation radicals, $E \approx 1.0$ V vs. Ag/AgCl), or deep blue (carbazole cation radicals, $E \geq 1.3$ V). The electrochromism is excellently reversible provided that the potential applied does not exceed 1.4 V and that the films are carefully protected against oxygen and moisture. The oxidized polymer films exhibit an additional strong absorption in the near-infra-red which can be ascribed to charge-transfer interactions between charged and uncharged dimer units or dimer and monomer carbazole units. The copolymer composition has little influence on the electrochemical properties but strongly affects the extent of the charge-transfer interactions. High carbazole concentrations favour the interactions considerably.

No indications were found for the existence of blue dicarbazolylmethyl cations, which had recently been proposed² to result from the reaction of carbazole cation radicals with dichloromethane solvent molecules. Instead Cz-PSi behaved identically in numerous solvents, such as dichloromethane, tetrahydrofuran, acetonitrile and propylene carbonate, making the formation of the cations highly unlikely. The intense blue colour occurring at higher potentials is rather due to the carbazole cation

Table 3 Peak oxidation potentials of electrochemical deposits of polymers 1–3

| Polymer | Potential (V) | (vs. Ag/AgCl) ^a |
|---------|---------------|----------------------------|
| 1 | 1.02 | 1.32 |
| 2 | 0.97 | 1.32 |
| 3 | 0.86 | 1.33 |

^aScan rate 20 mV s^{-1}

radical moiety, as also proposed by Shirota and coworkers^{3,8}. Obviously the extremely high reactivity of the cation radicals known from studies in solution⁶ is considerably diminished, if they are immobilized by chemical binding to a polymer backbone. On the other hand, they are still very reactive and are responsible for the rapid decomposition of the polymer in air and moisture, for example. In general, we believe that the redox behaviour of Cz-PSi described above and summarized in *Schemes 2 and 3* is transferable to other carbazole-containing polymers, e.g. poly(*N*-vinylcarbazole), and can also explain their electrochemical behaviour.

Our studies demonstrate that Cz-PSi can be utilized as electroactive materials in electrochromic displays or as conductive coatings provided that they are protected against environmental influences.

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