# Conductive properties of poly(4-vinylpyridine)–poly(dimethylsiloxane) block copolymers doped with tetracyanoquinodimethane

**Nihan Nugay, Zuhal Küçükyavuz* and Savaş Küçükyavuz**
*Middle East Technical University, Department of Chemistry, 06531 Ankara, Turkey*
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Poly(4-vinylpyridine)–poly(dimethylsiloxane) (P4VP–PDMS) block copolymers with various compositions were prepared by anionic polymerization. The 4VP block was quaternized with methyl iodide and reacted with 7,7′,8,8′-tetracyanoquinodimethane (TCNQ), which is in both anion radical ($TCNQ^{-\bullet}$) and neutral form ($TCNQ^0$). The products were then characterized by $^1H$ nuclear magnetic resonance and Fourier-transform infra-red spectroscopy, scanning electron microscopy and differential scanning calorimetry techniques. The electrical conductivities of processable and flexible films of these block copolymers were measured with the four-probe method and found to be as high as $10^{-2}\,S\,cm^{-1}$. The optimal $TCNQ^0$ doping for which the conductivities are highest were also determined.

**(Keywords: poly(4-vinylpyridine); poly(dimethylsiloxane); block copolymers; doping; four-probe method; electrical conductivity)**

## INTRODUCTION

The great need for electrically conductive polymers that are flexible and capable of being shaped by ordinary processes has stimulated much research activity[1]. Attempts have been made either to blend conductive polymers with conventional ones[2] or to synthesize block/graft copolymers in which one of the blocks consists of a potentially conducting polymer[3] while the other block is a polymer that increases the solubility in organic solvents of the entire copolymer and improves processability and mechanical properties. Besides, the formation of a continuous percolating phase of conductive polymers is needed to achieve conductivity throughout the sample[3].

Poly(vinylpyridine) polymers have been found attractive owing to their advantages in doping with iodine[4] or the organic electron acceptor 7,7′,8,8′-tetracyanoquinodimethane (TCNQ)[5,6] in the formation of a semiconductor. The latter is especially promising because an additional improvement of the conductivity is obtained by incorporation of unreduced TCNQ.

The present paper reports the electrical properties of poly(4-vinylpyridine)–poly(dimethylsiloxane) (P4VP–PDMS) block copolymers doped with TCNQ in different amounts. The environmental stability results of these studies are also presented.

## EXPERIMENTAL

### *Polymer synthesis and quaternization*

P4VP–PDMS block copolymers with various compositions were prepared via an anionic polymerization technique. Hexamethylcyclotrisiloxane was used as the siloxane monomer. The initiator was sodium naphthalene. 4VP was first completely polymerized for 3 h in pyridine/tetrahydrofuran (THF) mixture at −70°C. Then siloxane monomer in THF solution was introduced into the reactor and polymerized for 48 h at 25°C. The P4VP block in the copolymers was converted to polycation by complete quaternization with methyl iodide at 50°C under a nitrogen atmosphere. All quaternized block copolymers were completely soluble in water. Details of the polymer synthesis and quaternization reaction are included in a separate publication[7].

### *Synthesis of TCNQ simple salts of polymers*

Poly(1-methyl-4-vinylpyridinium-$TCNQ^{-\bullet}$) simple salts of block copolymers were prepared by the reaction of quaternized polymer with the lithium salt of TCNQ according to Lupinski's procedure[6]. A definite amount of quaternized sample was dissolved in water and mixed with a solution of LiTCNQ in water at room temperature. The reaction mixture was then stirred for an hour and the resultant dark blue precipitate was filtered, washed with methanol, water and ether, and dried under vacuum. Samples were stored in an inert atmosphere.

### *Film casting and formation of TCNQ complex salts of polymers*

A solution of a weighed amount of neutral TCNQ ($TCNQ^0$) and TCNQ simple salts of polymers in dimethylformamide (DMF) was cast in a flat Teflon mould. Casting was carried out *in vacuo* for more than 24 h at room temperature and resulted in black films of complex salts having 0.04–0.10 mm thickness.

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* To whom correspondence should be addressed

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### *Measurements*

Routine $^1H$ n.m.r. spectra were recorded on a Beckman 250 n.m.r. spectrometer in $CDCl_3$ and deuterated dimethylsulfoxide (d-DMSO). *FT*i.r. spectra of the samples were taken with a Nicolet DX-510 *FT*i.r. spectrometer using KBr pellets. Thermal measurements were carried out on a Perkin–Elmer DSC-7. The surfaces of the polymeric films were examined using a Cambridge Stereo Scan S4-10 model SEM equipped with an energy-dispersive analyser. Samples were used without a conductive coating. The conductivities of the polymer complexes were obtained using a four-probe conductivity cell (Kulucke and Soffa Ltd) having probes with 0.127 mm spacing. Voltage was measured with a Keithley Instruments 155 Null Detector–Microvoltmeter. The environmental stability of doped samples was studied by measuring the conductivities in the open atmosphere at room temperature for 30 days.

## RESULTS AND DISCUSSION

### *Sample characterization*

Some characteristics of the block copolymers are given in *Table 1*. In order to keep P4VP in the continuous phase in all the block copolymer samples, its mole percentage was held above 58%.

In *Figure 1*, the $^1H$ n.m.r. spectrum of PVPS 3 block copolymer is shown. At 8.4 and 6.5 ppm the characteristic peaks of 4VP ring protons[8] are observed. The peak at 0.15 ppm belongs to siloxane methyl-group protons[9]. Although the $\alpha$ and $\beta$ protons of the skeleton have one broad, single resonance peak centred at 1.5 ppm, as reported by Ghesquire[10], the presence of two separate signals in this area can be assigned to the existence of a connected PDMS sequence having an electropositive Si atom, which causes a shift of the peak to higher field. The presence of both P4VP and PDMS sequences in the product is evidence of block copolymer formation. In addition, PDMS is known to be water-insoluble. The non-existence of precipitation or phase separation during dissolution of the quaternized samples in water also excludes the probability of formation of homopolymer mixtures.

**Table 1** Some characteristics of P4VP–PDMS block copolymers

| Sample | Composition (mol% P4VP) | $T_{g1}$[a] (°C) | $T_{g2}$[b] (°C) |
|---|---|---|---|
| PVP | 98 | – | 152 |
| PVPS 5 | 93 | −130 | 151 |
| PVPS 2 | 84 | −130 | 152 |
| PVPS 1 | 71 | −130 | 150 |
| PVPS 4 | 64 | −130 | 142 |
| PVPS 3 | 58 | −130 | 135 |

[a] Glass transition temperature of soft block (PDMS)
[b] Glass transition temperature of hard block (P4VP)

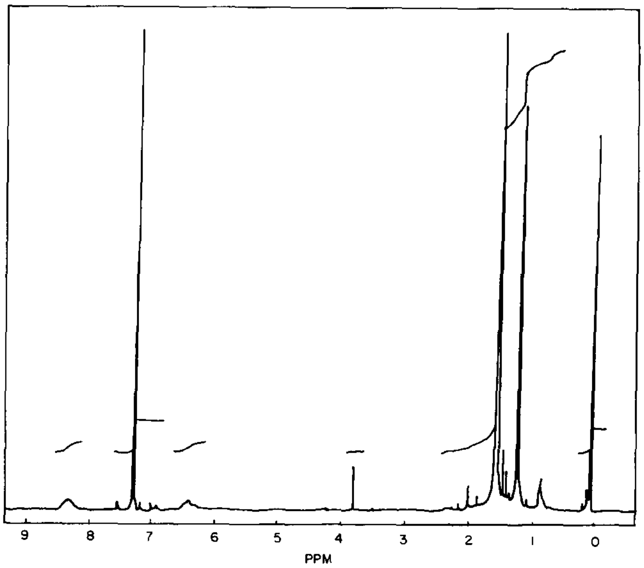


**Figure 1** $^1H$ n.m.r. spectrum of PVPS 3 block copolymer taken in $CDCl_3$ without external reference (tetramethylsilane, TMS)

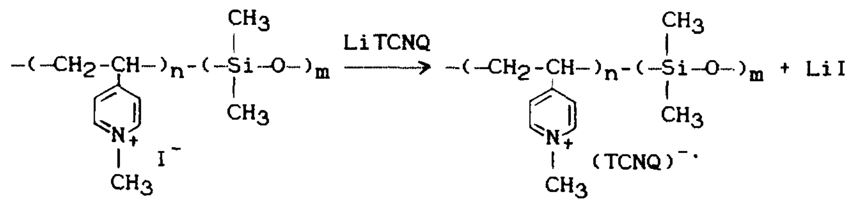
**Table 2** Preparation of polymeric TCNQ simple salts

| Sample | Polycation (g) | LiTCNQ (g) | Time (h) | Yield (%) |
|---|---|---|---|---|
| PVPSQD 5 | 0.2 | 0.2 | 1 | 94 |
| PVPSQD 2 | 0.2 | 0.2 | 5 | 94 |
| PVPSQD 1 | 0.4 | 0.4 | 1 | 98 |
| PVPSQD 4 | 0.2 | 0.2 | 3 | 97 |
| PVPSQD 3 | 0.2 | 0.2 | 5 | 97 |
| PVPQD | 0.3 | 0.3 | 4 | 98 |

Following the quaternization with methyl iodide, the samples were then reacted with LiTCNQ to get a simple salt according to *Scheme 1*. In this treatment, water was used as the reaction solvent, because analysis of the polymeric TCNQ salt using different polycations[6] has indicated that there remains very little of the original counterions (halide or sulfate) when aqueous solutions are used; however, solvents such as ethylene glycol and alcohol sometimes afford products that still retain an appreciable fraction of these ions.

Results of the preparation of simple salts of quaternized block copolymers are given in *Table 2*. The yield values ranging from 94% to 98% showed that there is about 2–6% iodine left in the resultant charge-transfer complex.

Energy-dispersive X-ray analysis (EDX) data of the quaternized sample (PVPSQ 2) and its simple salt (PVPSQD 2) are interpreted in *Figure 2*. The intense peaks at 3.94 and 4.22 Å, which are the characteristic L X-ray emission lines ($L\alpha_2$: 3.93; $L\beta_{1,2}$: 4.22) of iodine[11], have almost disappeared in the simple salt spectrum. This is further evidence of $I^-/TCNQ^-$ exchange.



**Scheme 1**

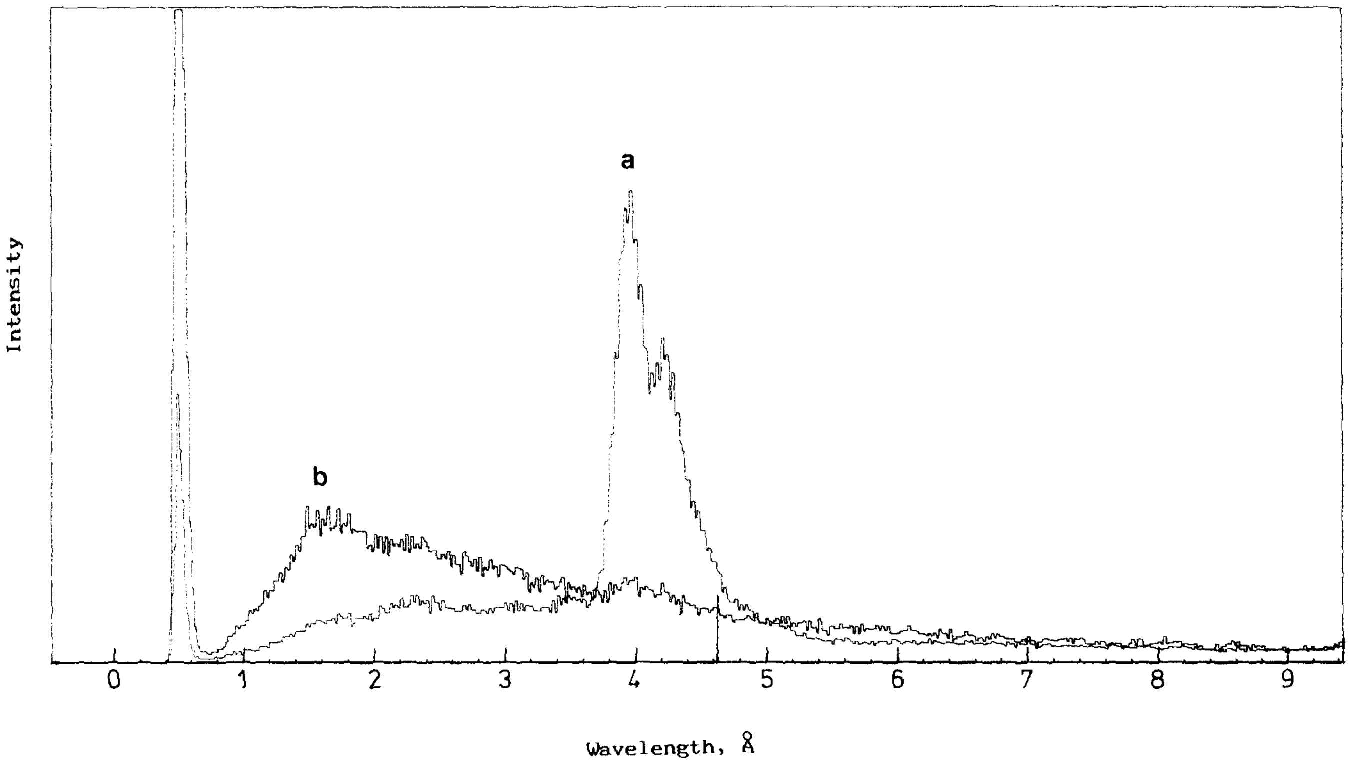


**Figure 2** EDX spectra of PVPSQ 2 (a) and PVPSQD 2 (b) samples

*Figure 3* represents the *FT*i.r. spectrum of PVPS 2 sample, and *Figure 4* shows the spectrum of PVPSQ 2 together with that of PVPSQD 2 simple salt. The spectrum of the former (*Figure 3*) exhibits stretching bands assigned to the pyridine ring[8] at 1600, 1560, 1490 and 1420 cm$^{-1}$. After quaternization of the P4VP block in the copolymer (*Figure 4a*), two bands at 1640 and 1510 cm$^{-1}$ corresponding to quaternized pyridine ring and the characteristic band of iodine at 580 cm$^{-1}$ (ref. 8) appeared, whereas the bands of unquaternized pyridine ring at 1560 and 1420 cm$^{-1}$ disappeared, showing complete quaternization[12]. In the infra-red absorption spectrum of PVPSQD 2 simple salt (*Figure 4b*), a broad –CN absorption band at 2170–2197 cm$^{-1}$ and non-existence of iodine absorption indicate the formation of TCNQ salt with polycation as reported by Acker[13].

$^1$H n.m.r. spectra of PVPSQ 2 and PVPSQD 2 samples and of LiTCNQ are given in *Figure 5*. The shift of 8.4 and 6.5 ppm peaks of the block copolymer (*Figure 1*) to lower field (8.8 to 7.9 ppm) and the appearance of an additional peak at 4.34 ppm, which belongs to protons of the methyl group connected to the nitrogen[14], are characteristic of the quaternized sample spectrum (*Figure 5a*). This shift is most probably due to the strong ionic interaction, which results in a decrease of electron density on ring protons, and then causes less shielding and resonance of them at lower field. After TCNQ exchange (*Figure 5b*), all of these protons resonated at higher field (8.6, 7.3 and 4.22 ppm), which can be attributed to weaker ionic interaction in this case owing to the steric factor. Besides, the 7.6 and 6.8 ppm peaks of ring protons of TCNQ anion, which is given in *Figure 5c*, appeared in the same spectrum.

*Figure 6* gives the d.s.c. traces of PVPS 2 and PVPSQD 2 simple salt. Trace (a), which was obtained for the pure P4VP segment in the block copolymer, shows the glass

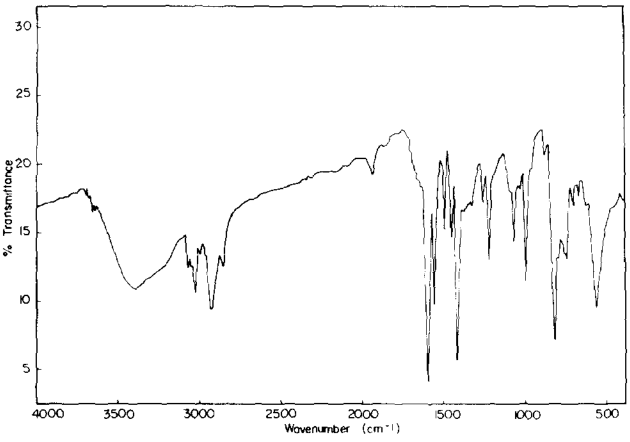


**Figure 3** *FT*i.r. spectrum of PVPS 2 sample taken with KBr pellet

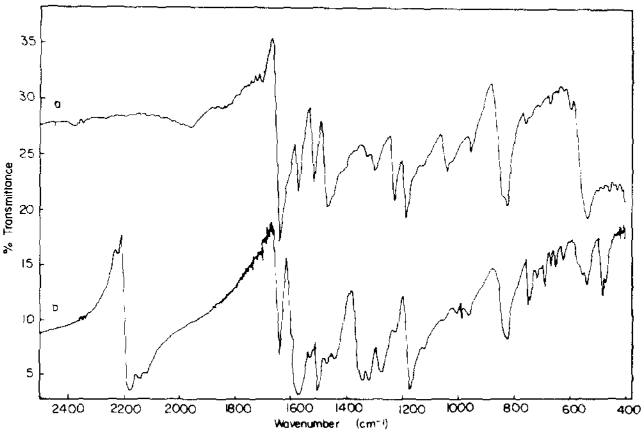


**Figure 4** *FT*i.r. spectra of PVPSQ 2 (a) and PVPSQD 2 (b) samples taken with KBr pellet

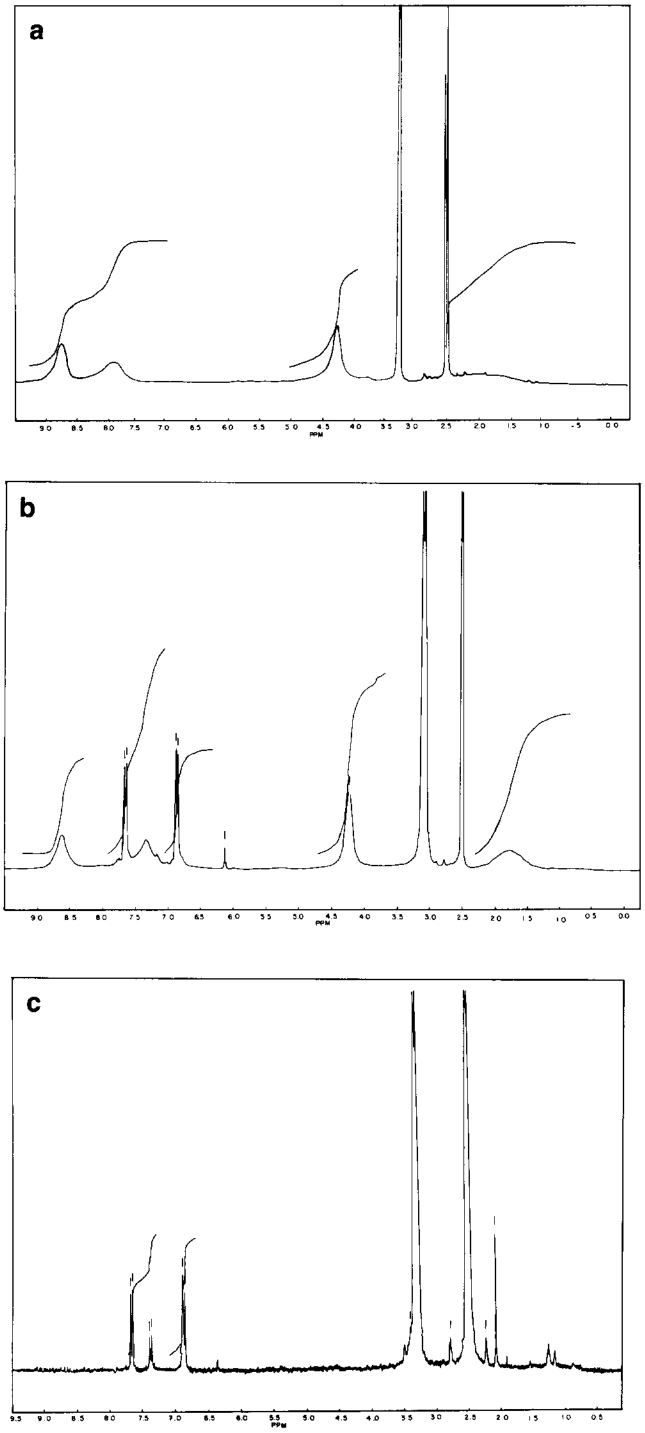


**Figure 5** $^1$H n.m.r. spectra of PVPSQ 2 (a), PVPSQD 2 (b) and LiTCNQ (c) in d-DMSO

transition at 152°C as reported[15]. The transition of polymeric conductive TCNQ simple salt (trace (b)) is lower (145°C) than the $T_g$ of pure P4VP, which may be an indication of partial degradation of the polymer, but may also be due to the plastifying effect of iodine left in the structure[16].

SEM micrographs of the surfaces of the PVPSQ 2 and PVPSQD 2 simple salt at the same magnifications are shown in *Figure 7*. It is known that, in order to obtain a picture of the local surface of an insulating polymer in SEM investigations, a conductive coating is necessary. Here, these images for two uncoated samples indicate the sufficiently conductive nature of the films, providing high scattering contrast. The light regions originate from the microphase of electron-rich P4VP-I complex (a). These electron-rich regions get larger and more stable in the case of P4VP–TCNQ complex (b), which is more conductive than the former.

*Conductivity measurements*

The measured conductivities of doped polymeric TCNQ simple salts are tabulated in *Table 3*. The conductivities of block copolymers as well as those of P4VP were of the order of $10^{-15}$ S cm$^{-1}$. After the quaternization of the P4VP block in the copolymers, conductivity values increased to $10^{-5}$ S cm$^{-1}$. It seems from *Table 3* that conductivities of simple salts are not much affected by the existence of the insulating PDMS block in the copolymers. This is an expected result, since all block copolymers show a continuous P4VP phase, resulting in a greater number of charge carriers per unit volume in the major component for electron transport[17].

Some polymeric TCNQ complex salts were prepared by doping neutral TCNQ into the simple salts of the block copolymer as given in *Scheme 2*.

*Figure 8* shows the effect of TCNQ$^0$ content on the conductivity of the PVPSQD 1 sample. As the content of neutral TCNQ is raised, conductivity increases, with a maximum at about 30% TCNQ$^0$ doping, and then decreases, suggesting that in the complex salt there is an optimal amount of TCNQ$^0$ where the conductivity is

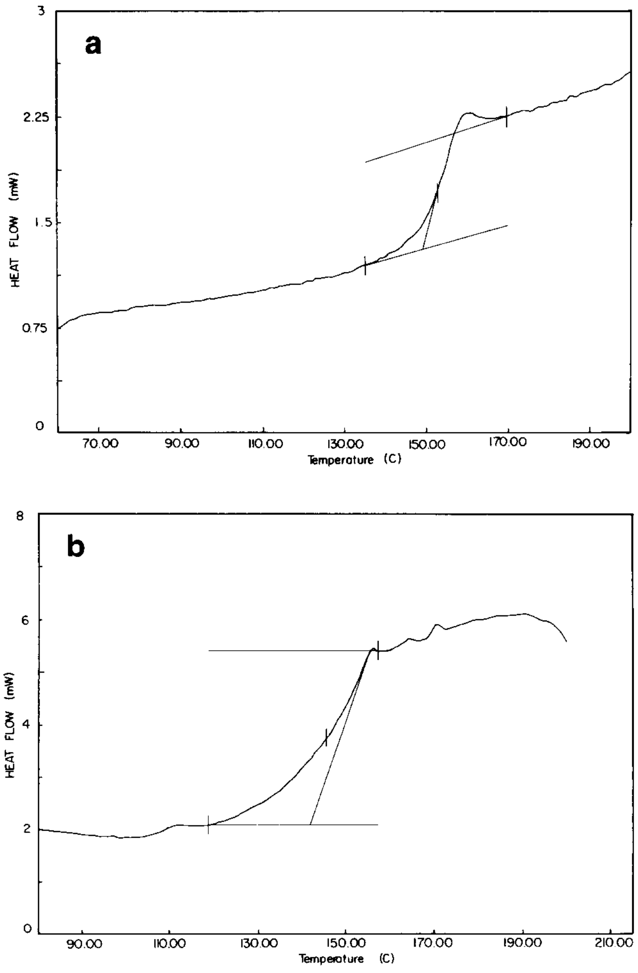
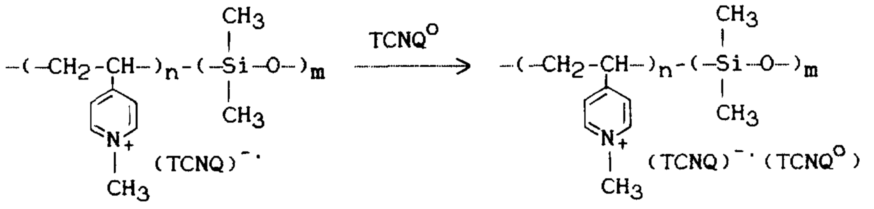


**Figure 6** D.s.c. thermograms of PVPS 2 (a) and PVPSQD 2 (b) samples



**Scheme 2**

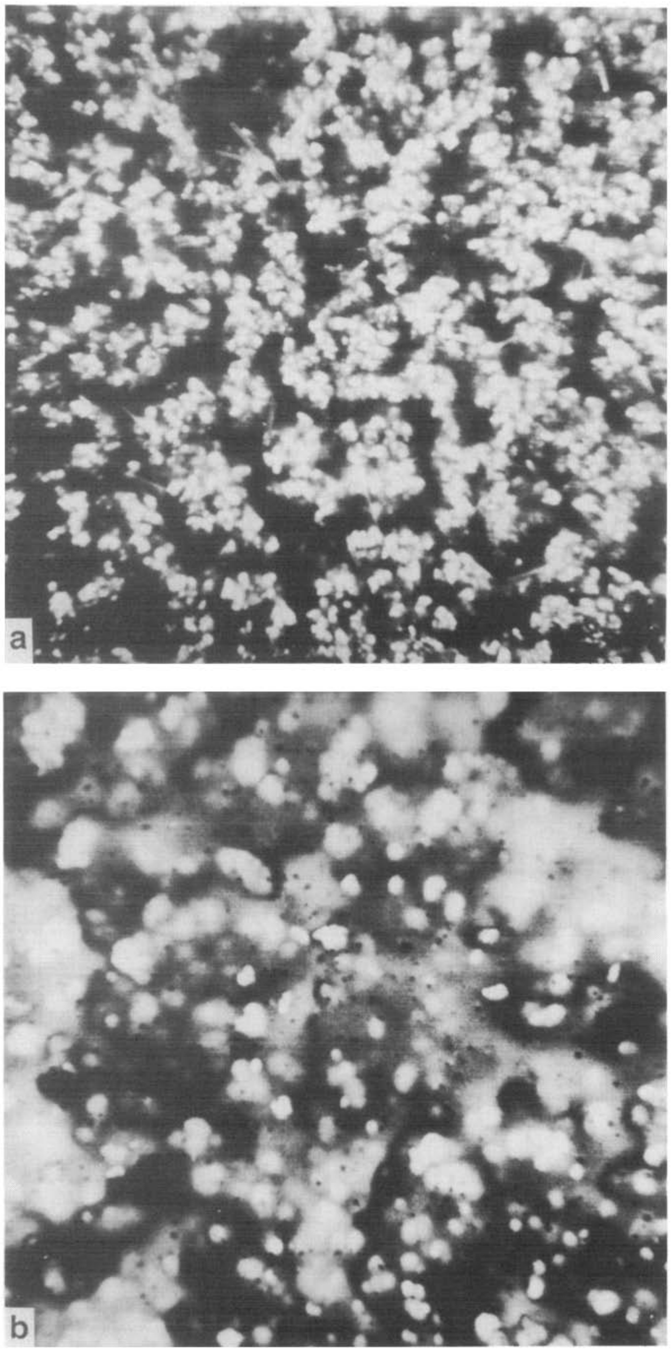


**Figure 7** SEM micrographs of PVPSQ 2 (a) and PVPSQD 2 (b) samples (magnification ×2000)

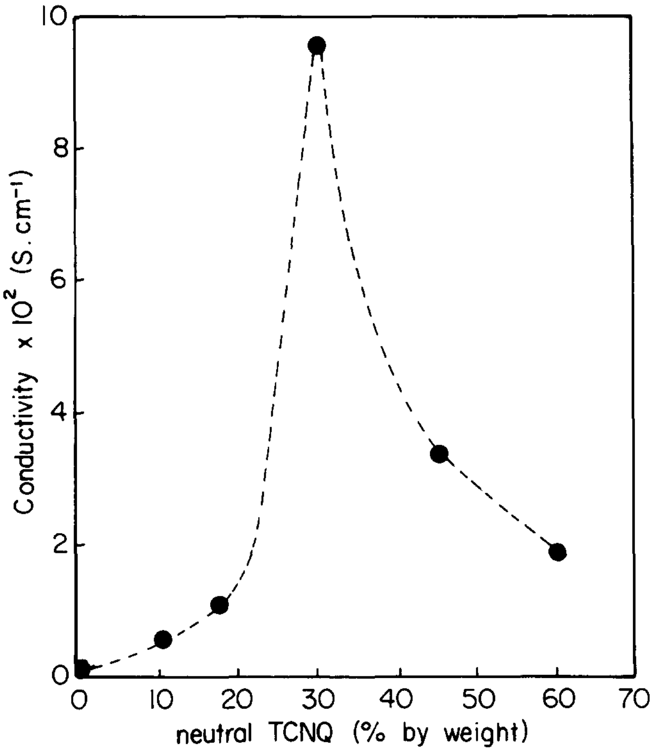


**Figure 8** Conductivity of PVPSQD 1 complex salt as a function of added neutral TCNQ

**Table 3** Conductivities of polymeric TCNQ simple salt

| Sample | Conductivity, $\sigma$ (S cm$^{-1}$) |
|---|---|
| PVPQD | $4.1 \times 10^{-3}$ |
| PVPSQD 5 | $4.1 \times 10^{-3}$ |
| PVPSQD 2 | $3.3 \times 10^{-3}$ |
| PVPSQD 1 | $1.3 \times 10^{-3}$ |
| PVPSQD 4 | $1.7 \times 10^{-3}$ |
| PVPSQD 3 | $1.1 \times 10^{-3}$ |

highest. This strong dependence of conductivity of complex salts on the amount of neutral TCNQ was also reported by some other researchers[18–20]. These latter made two proposals: either (i) TCNQ molecules are associated with P4VP cations, forming stacks of alternating charged and neutral TCNQ molecules; or (ii) TCNQ molecules are packed almost randomly in the polycation network, so that with the interaction of TCNQ anion radicals with $TCNQ^{-\bullet}$ or $TCNQ^0$ in nearby positions, the electrons may delocalize transiently in the TCNQ aggregates thus formed in the occurrence of either a charge-transfer state ($TCNQ^0 \cdots\cdots TCNQ^{2-}$) or a charge-resonance state ($TCNQ^{-\bullet} \cdots\cdots TCNQ^0 \leftrightarrow TCNQ^0 \cdots\cdots TCNQ^{-\bullet}$).

## *Environmental stability studies*

The chemical and electrical stabilities of polymeric TCNQ complex salts have been studied previously[21]; it was found that $TCNQ^{-\bullet}$ in the complex salt decomposed to α,α-dicyano-*p*-toluoylcyanide as the final product, and that water played an important role in the reaction.

**Table 4** Conductivity change of TCNQ simple salt of PVPSQD 1 with time under vacuum

| Time (days) | Conductivity ($S\,cm^{-1}$) |
|---|---|
| 0 | $1.3\times10^{-3}$ |
| 13 | $1.3\times10^{-3}$ |
| 16 | $1.3\times10^{-3}$ |

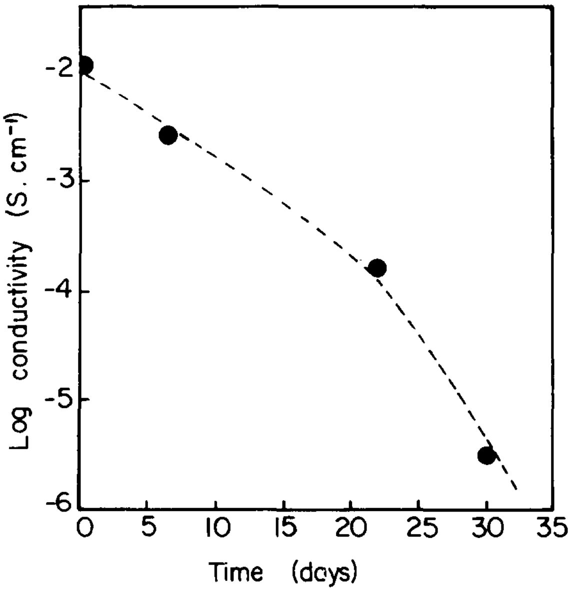


**Figure 9** Conductivity change in PVPSQD 1 complex salt having 60% neutral TCNQ as a function of time in the open atmosphere

Prepared simple salts were stored under vacuum just before the preparation of complex salts within 24 h. The observed stability of these salts was important in making certain that the conductivity of the sample, which has already been gained by TCNQ anion radical, was not lost. *Table 4* shows the unchanged conductivity data for PVPSQD 1 simple salt during 16 days under vacuum.

The results of the conductivity change in the open atmosphere for PVPSQD 1 complex salt doped with 60% $TCNQ^0$ are represented in *Figure 9*. The conductivity of the complex salt decreases from $10^{-2}$ to $10^{-6}\,S\,cm^{-1}$ within 30 days in the open atmosphere and at room temperature. The change in conductivity is probably due to the loss of unpaired electrons as a result of the decomposition of $TCNQ^{-\bullet}$ as described above in the presence of water[21].

## CONCLUSION

This work demonstrated that it is possible to prepare conductive, processable and soluble polymers with improved mechanical properties via TCNQ modification of P4VP–PDMS block copolymers.

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