Conducting properties of iodine-doped poly(4-vinylpyridine)–poly(dimethylsiloxane) block copolymers

Nihan Nugay, Zuhal Küçükyavuz* and Savas Küçükyavuz
Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey

(Received 12 November 1992; revised 30 April 1993)

Block copolymers of various compositions, consisting of poly(4-vinylpyridine) (P4VP) and poly(dimethylsiloxane) (PDMS) blocks, were prepared by anionic polymerization. These samples were modified by the addition of various amounts of iodine in solution. The electrical conductivities of the doped materials were measured by the four-probe method and were found to be as high as 10^{-5} S cm^{-1}. The optimum ratio of iodine to pyridine which gave the highest conductivity was determined.

(Keywords: poly(4-vinylpyridine); poly(dimethylsiloxane); block copolymers)

INTRODUCTION

A large number of studies have been carried out with the objective of preparing two-phase polymer systems, either in the form of blends[1,2] or as block/graft copolymers[3,4], in which one of the phases was formed by a polymer capable of being doped to achieve electrical conductivity. The main aim of this work is to circumvent the inherent insolubility, intractability and mechanical fragility of the conducting polymers that are presently available[5]. In addition, of principal interest in these studies are the need and requirements for the formation of a continuous percolating phase of the conducting polymer, which is required to achieve conductivity through the sample.

The present study is concerned with the electrical properties of P4VP–PDMS block copolymers in which the P4VP forms a continuous phase. Poly(4-vinylpyridine) and poly(dimethylsiloxane) are particularly good choices for the components of a block copolymer system: P4VP can be doped with I_2 to obtain a semiconductor with conductivities $\approx 10^{-4}$–10^{-7} S cm^{-1} (depending on the method of preparation[6]), and, in addition is prepared by anionic polymerization[7], which is necessary for preparation of well defined block copolymers, whereas the presence of PDMS segments in the blocks offers potentially favourable properties such as low T_g, high thermal and oxidative stability and low surface energy[8].

EXPERIMENTAL

Polymer synthesis

P4VP–PDMS block copolymers with various compositions were synthesized by sequential anionic polymerization using sodium naphthalene as the difunctional initiator. First, the 4-vinylpyridine was completely polymerized in a pyridine/tetrahydrofuran (THF) mixture at -70°C for 3 h. Siloxane monomer (hexamethylcyclotrisiloxane) in THF was then introduced into the reaction vessel and polymerized for 48 h at 25°C. Details of the polymer synthesis are reported elsewhere[9]. Concentrations of the monomers and the initiator have been correctly adjusted so that the number-average molecular weights of the resulting block copolymers are $\approx 2.5 \times 10^5$ g mol^{-1}.

Preparation of iodine complexes of the polymers

Complexes of P4VP–PDMS block copolymers, with I_2/pyridine unit mole ratios of 1.0, 1.5, 2.0, and 3.0, were prepared in dichloromethane solution at room temperature. Weighed amounts of iodine were added to dilute solutions (3% wt/vol) of the block copolymers, with continuous mixing over a period of 5 min, under a nitrogen atmosphere. Casting of the resultant products in flat Teflon moulds, carried out at room temperature under a nitrogen atmosphere over a period of 24 h, resulted in films having thicknesses of 0.07–0.12 mm.

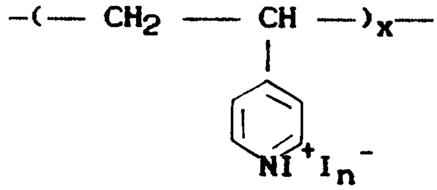
Sakai *et al.*[10] have suggested the following reactions to occur between pyridine (Py) and I_2 in polar solvents:

$$\mathrm{Py} + \mathrm{I_2} \rightarrow \mathrm{PyI_2} \qquad \text{(outer complex)}$$

$$\mathrm{PyI_2} \rightarrow (\mathrm{PyI})^+ + \mathrm{I}^-$$

$$(\mathrm{PyI})^+ + \mathrm{I}^- + \mathrm{PyI_2} \rightarrow \mathrm{I_3^-} + (\mathrm{Py_2I})^+ \qquad \text{(inner complex)}$$

It is generally accepted that P4VP can form the same type of charge transfer complex with iodine, similar to that also found with poly(2-vinylpyridine) (P2VP)[11], and which has the following structure:



The environmental stability of the doped materials was studied by measuring the conductivity changes in samples

---

* To whom correspondence should be addressed

0032-3861/94/020243-03

which had been left both in the open atmosphere and in vacuum at room temperature, over periods of 24 and 120 h, respectively. Non-bound iodine values for these samples were determined by simple weight loss calculations.

Measurements

For the conductivity measurements, film samples were mounted in a four-probe conductivity measurement cell (Kulucke and Soffa Ltd.) which had probes with spacings of 0.127 mm. Voltage was measured with a Keithley Instruments 155 null detector microvoltmeter. The conductivities were calculated according to the following relationship[12]:

$$\sigma\ (\mathrm{S\,cm^{-1}}) = \frac{I}{VWF^*} \qquad (1)$$

where I is the current (A), V is the voltage (V), W is the sample thickness (cm) and F^* is a correction factor (which in this case has a value of 4.532).

The glass transition behaviour of both the block copolymers and their iodine complexes were examined by using a Perkin–Elmer DSC-7 differential scanning calorimeter operating at a heating rate of 20°C min^{-1}.

RESULTS AND DISCUSSION

The characteristics of the various block copolymers and the corresponding iodine doped materials are given in *Table 1*. The polymer–iodine complexes have a stoichiometry in which two molecules of iodine interact with each pyridine ring in the P4VP chain.

In general the conductivities of the samples change from 10^{-5} to 10^{-6} S cm^{-1} with an increase in the PDMS content of the block copolymers in which the P4VP forms the continuous phase. In principle, if the conducting phase is continuous, the conductivities should be only slightly lower than those of the corresponding homopolymer system because of the greater number of charge carriers per unit volume of the major component available for electron transport[13].

Table 1 Characteristics of the various block copolymers and corresponding iodine-doped samples (I_2/pyridine unit = 2)

Copolymer sample	P4VP content[a] (mol%)	Conductivity (S cm^{-1})
I-PVP	98	9.2×10^{-5}
I-PVPS 5	93	3.6×10^{-5}
I-PVPS 2	84	4.0×10^{-5}
I-PVPS 1	71	9.5×10^{-6}
I-PVPS 4	64	6.0×10^{-6}
I-PVPS 3	58	3.0×10^{-6}

[a] Determined by using the Kjeldahl nitrogen analysis technique before doping with iodine

Table 2 Conductivity changes after removal of the non-bonded iodine in the doped block copolymers

	In open atmosphere		Under vacuum	
Copolymer sample	Weight loss (%)	Conductivity (S cm^{-1})	Weight loss (%)	Conductivity (S cm^{-1})
I-PVP	7.6	4.7×10^{-5}	22.5	5.5×10^{-6}
I-PVPS 5	8.9	1.3×10^{-5}	26.1	8.8×10^{-6}
I-PVPS 2	16.9	1.5×10^{-5}	34.1	9.7×10^{-6}
I-PVPS 1	19.0	4.4×10^{-6}	42.2	1.7×10^{-6}

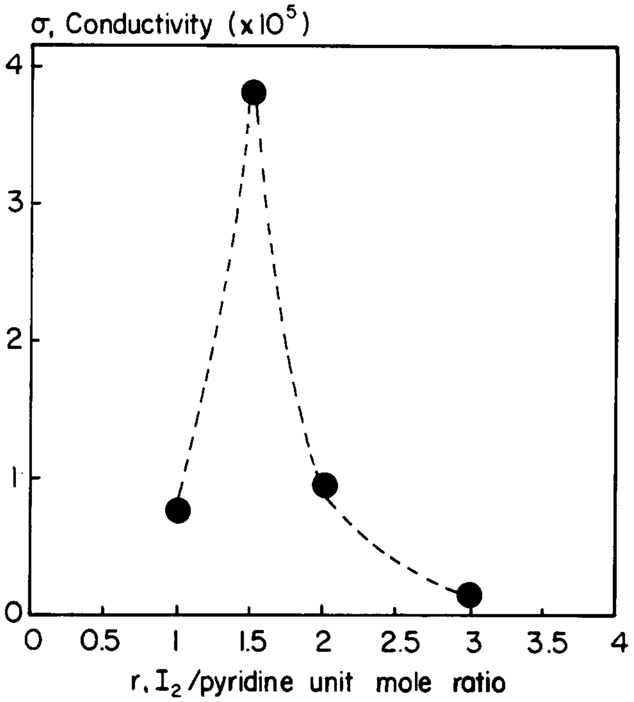


Figure 1 Effect of the I_2/pyridine unit mole ratio on the conductivity of the I-PVPS 1 doped copolymer sample

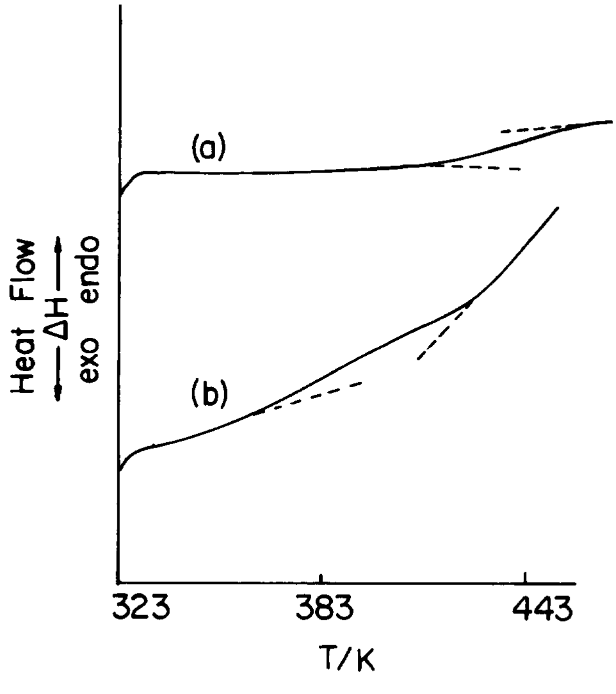


Figure 2 D.s.c. thermograms of the PVPS 1 block copolymer sample, before and after treatment with iodine: (a) untreated sample and (b) iodine-doped sample

The effect of the amount of iodine on the conductivities of these doped block copolymers was followed by using complexes having different I_2/pyridine unit mole ratios, and the results are shown in *Figure 1*. The maximum conductivity that could be achieved was found to be ≈3.8×10^{-5} S cm^{-1}, for a sample with a mole ratio of 1.5. Similar results were also reported by Möller and Lenz[14] and by Philips and Unterecker[15] who found that the conductivities of the P2VP–I_2 system decreased at both higher and lower levels of iodine.

Table 2 shows the conductivity changes in films which had been stored both in the open atmosphere and under vacuum. The conductivities dropped to $\approx 10^{-6}$ S cm^{-1} after non-bonded iodine was removed, especially under vacuum conditions, but these conductivities are still much higher than those of pure P4VP and PDMS ($\approx 10^{-15}$ S cm^{-1})[6]. This decrease in conductivity may be explained by a distortion of the iodine crystalline lattice caused by loss of the non-bonded iodine[11].

Figure 2 gives the d.s.c. thermograms of the PVPS 1 block copolymer sample both before and after treatment with iodine. The upper trace, which was obtained for the pure block copolymer, shows a glass transition at 152°C for the P4VP phase, as previously reported in the literature[16]. The lower trace shows the thermal behaviour of the polymer after it was deposited from an iodine-containing methylene chloride solution and contained an I_2/pyridine mole ratio of 2.0. The glass transition in this is much lower and broader than the T_g of the pure P4VP segment of the undoped block copolymer. This might be an indication of partial degradation of the polymer but may also be due to the plasticizing effect of iodine, which has been also reported by Möller and Lenz[14] for iodine-doped P2VP samples.

CONCLUSIONS

Iodine complexes of P4VP–PDMS block copolymers were prepared which exhibit interesting semiconductor properties, with maximum conductivities $\approx 10^{-5}$ S cm^{-1}. The presence of an elastomeric 'insulating' PDMS segment in these samples does not greatly affect the conductivity, whereas it does improve the mechanical and thermal properties of the conducting structure.

As a next step, modification of these block copolymers with tetracyanoquinodimethane (TCNQ) appears to be a particularly promising way to achieve higher conductivities, along with improved physical properties.

REFERENCES

1 Galvin, M. E. and Wnek, G. E. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prep.* 1984, **25**, 229

2 Galvin, M. E. and Wnek, G. E. *Polym. Commun.* 1982, **23**, 795

3 Leek, I. and Jopson, H. *Polym. Bull.* 1983, **10**, 105

4 Ikeno, S., Yokoyama, M. and Mikawa, H. *Polym. J.* 1978, **10**, 123

5 Aldissi, M. *Polym. Plastics Tech. Eng.* 1987, **26**, 145

6 Mainthia, S. B., Kronick, P. L. and Labes, M. M. *J. Chem. Phys.* 1964, **41**, 2206

7 Smid, J. and Szwarc, M. *J. Polym. Sci.* 1962, **61**, 31

8 Küçükyavuz, S., Küçükyavuz, Z. and Erdogan, G. *Polymer* 1990, **31**, 379

9 Nugay, N., Küçükyavuz, Z. and Küçükyavuz, S. *Polym. Int.* 1993, **32**, 93

10 Sakai, H. M., Maeda, Y., Ichiba, S. and Nagita, H. *J. Chem. Phys.* 1980, **72**, 6192

11 Stankovic, R. I., Lenz, R. W. and Karasz, F. E. *Eur. Polym. J.* 1990, **26**, 359

12 Runyan, V. R. 'Semiconductor Measurements and Instrumentation', McGraw-Hill, New York, 1975

13 Pascal, M., Lingelsel, P. and Gallot, Y. *Makromol. Chem.* 1987, **183**, 2907

14 Möller, M. and Lenz, R. W. *Makromol. Chem.* 1989, **190**, 1153

15 Philips, G. M. and Unterecker, D. F. *Proc. Electrochem. Soc.* 1980, **80**, 195

16 Schulz, R. C., Schwarzenbach, E. and Zöller, J. *Polym. Prepr.* 1988, **29**, 144