NOTE

Conductive Polymer Thermoelements

INTRODUCTION

Conductive polymeric films, obtained by reticulate doping with organic charge transfer (CT) complexes or conductive salts, show many interesting properties.[1] Characteristic for these materials is a low percolation threshold. Relatively high electrical conductivity, on the order of 10^{-2} s/cm, can be achieved for the additive concentration that is even less than 1 wt % of polymer. Reticulate-doped films are transparent and their mechanical properties are not changed as compared to the films prepared with pure polymer. Since a conductive network in the polymer matrix is formed of fine crystalline CT complex structures, the electrical properties of reticulate-doped polymers are dependent on the type of CT complex used and on the morphology of the crystallites. The modifications of the reticulate doping method allow the films showing not only isotropic bulk conductivity, but also anisotropic conductivity and surface conductivity, to be obtained. This makes possible a tailoring of systems showing versatile physical and geometrical properties.

It has been discovered that conductive reticulate doped polymers are characterized by different values of Seebeck coefficient, depending on the nature of the complex forming conductive network.[2]

The temperature dependencies of the Seebeck coefficient do not show any discontinuities or extremes that are attributed to the phase transitions that are characteristic for single crystals of CT complex or salt used. This is due to the presence of the defects in the microcrystalline conductive network, which are responsible for the smearing of the phase transitions.

The properties of the reticulate-doped films mentioned above make possible the application of these materials for preparation of flat, fully organic devices, which can be used for measuring the temperature basing on the thermoelectric effect, that is, polymeric thermocouples. Polymer films show low thermal conductivity. In this article, we present the results of our preliminary studies on this subject.

EXPERIMENTAL

The studies were performed on the 10–20 μm thick polymer films bulk conductive and surface conductive, obtained by different methods:

1. PC + 2 wt % of BEDT-TTF_2J_3, surface conductive,[3]
2. PMMA + 0.8 wt % of BIPA$(TCNQ)_2$, bulk conductive,[4]
3. PC + 1 wt % of DIPS-$J_{2.28}$, surface conductive,[5] and
4. PC + 2 wt % of TTF-TCNQ, surface conductive.[1]

The heterojunctions of strips of conductive reticulate-doped films for thermoelectric measurements were prepared by three methods: (1) pressing together, (2) joining the films with silver paint, and (3) sticking the films initially swelled with methylene chloride.

The junction of the polymer film/Au layer, evaporated on the polymer film surface, was also investigated. In case of the surface conductive films, the gold was evaporated on the same side on the conductive and nonconductive parts of the film surface. Such an Au/reticulate-doped polymer thermocouple consists of one strip of polymer film. In all cases, the reference junctions were made by joining the copper thin wires to the ends of the samples, using silver paint.

Studies of the dependencies of the thermopower on temperature were performed, using specially constructed jails. The thermoelectric power for a given temperature gradient was registered simultaneously for the reference standard thermocouple Cu/Constantan, using the electrometer Keitlhey 195A. The reference junctions were kept at 0°C.

RESULTS AND DISCUSSION

The measurements of thermoelectric properties of polymeric thermocouples were performed in the temperature range of −80°C to +80°C. It was found that for all investigated systems, the temperature dependences of the thermopower are close to linear, as is the case for commonly used metallic thermocouples. The values of the thermoelectric power at 25°C, for thermocouples composed of different pairs of conductive polymers, are presented in Table I. It is evident that some of the polymeric thermocouples show higher sensitivity as compared with Cu/Constantan.

The thermoelectric properties of the thermoelements, involving two given reticulate-doped polymers, were practically independent as to the method of their preparation. It was noted, however, that the method of the junction preparation, based upon the use of silver paint, cannot be used in cases where the films contain iodine as an acceptor. In such cases, the measurements are difficult after a few

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Table I Values of Thermoelectric Power at 25°C (in mV, Reference Junction at 0°C) for Different Couples of Reticulate Polymers and for Polymer Films with Evaporated Au Layer[a]

Material	Au	I	II	III	IV
Au	—	−0.72	1.61	0.43	0.09
I	−0.72	—	2.61	1.15	0.84
II	1.61	2.61	—	1.20	1.53
III	0.43	1.15	1.20	—	0.35
IV	0.09	0.84	1.53	0.35	—

[a] Symbols I–IV correspond to those in the Experimental section. (The values of thermoelectric power of Cu/Constantan and Fe/Constantan thermocouples at this temperature are 1.01 mV and 1.27 mV, respectively.)

days because of the noise that arises because of the increase in the sample resistivity, caused by the reaction of the iodine with silver.

It can be noted in Table I that in some cases the thermopower for a given couple of reticulate polymers is slightly higher, as compared to the sum of the thermopowers measured for thermocouples made of each of the two polymers with Au (compare, for example, I/II and I/Au + II/Au). Since reticulate-doped polymer films form ohmic contacts with Au and with each other, the explanation for these results requires further study.

CONCLUSIONS

It was shown that heterojunctions of different reticulate-doped polymers show interesting thermoelectric properties: the temperature dependencies of the thermopower are close to linear and in many cases the values of the thermopower are higher, as compared with the commonly used metallic thermocouples.

The method of obtaining the surface conductive films allows the printing of conductive areas of any shape on one or both sides of polymer film. Using such systems, it is possible to prepare relatively thin (less than 40 μm), flat thermocouples for special use for measuring the gradients of temperature between flat surfaces.

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